Supporting information for:

Fluorometric sensor based on bisterpyridine metallopolymer: Detection of cyanide and phosphates in water.

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Figure S1. $^1$H NMR (CD$_3$OD, 400 MHz) of 1 and 2.

Figure S2. Left: SEC trace of 1. Right: MALDI-TOF MS spectrum of 1.
Figure S3. Emission spectra of 2 (water, c = 5.8 \times 10^{-8} \text{ M}, \lambda_{ex} = 400 \text{ nm}) upon addition of NaOAc (water, c = 11.6 \mu\text{M} or 0.116 \text{ mM}).

Figure S4. $^1$H NMR a) 1 (CD$_3$OD, 400 MHz), b) 2 (CD$_3$OD, 400 MHz), c) 2 upon addition of 50 equivalents Na$_3$PO$_4$ (D$_2$O, 200 MHz).
Figure S5. UV-Vis absorption spectra ($10^{-6}$ M, water) of 1 and 2, upon addition of KCN.

Figure S6. Emission spectra of 2 (water, $c = 5.8 \times 10^{-8}$ M, $\lambda_{ex} = 400$ nm) upon addition of NaOH or H$_3$PO$_4$ (water, $c = 11.6$ $\mu$M).
Figure S7. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz) of 2 upon addition of one equivalent NaOH.

**Calculation of the dissociation constants**

The dissociation constants for the complex AB$_n$ of analyte (B) by fluorophore (A) were calculated from Eq. S1.\textsuperscript{1,2}

\[
A + nB \leftrightarrow AB_n
\]

\[
K_d^n = \frac{[A][B]^n}{[AB_n]}
\]

(Eq. S1)

When $[A]_0 = [A] + [AB_n]$ is the initial concentration of A and $[B]_0$ the initial concentration of B. Therefore:

\[
K_d^n = \frac{([A]_0 - [AB_n])[B]^n}{[AB_n]} \quad \text{and} \quad [AB_n] = \frac{[A]_0[B]^n}{K_d^n + [B]^n}
\]

(Eq. S2)

If $I_A$ and $I_{ABn}$ are the proportional constants for the fluorescence intensity:

$F_0 = I_A[A]_0$ and $F_{\text{end}} = I_{ABn}[A]_0$
\[ F_x = I_d[A] + I_{AB}[AB_n] \]
\[ = I_d([A_0] - [AB_n]) + I_{AB}[AB_n] \]
\[ = I_d[A_0] + (I_{AB_n} - I_d)[AB_n] \]
\[ = I_d[A_0] + (I_{AB_n} - I_d) \left( \frac{[B]^n}{K_d^n + [B]^n} \right) \]
\[ = F_0 + \frac{(F_{\text{end}} - F_0)[B]^n}{K_d^n + [B]^n} \]  
(Eq. S3)

What can also be written as Eq. 1 or Eq. S4.

\[ \frac{F_0 - F_x}{F_x - F_{\text{end}}} = \left( \frac{[B]}{K_d} \right)^n \]  
(Eq. S4)

The plot of log\([F_0 - F_x]/[F_x - F_{\text{end}}]\) vs. log[B] provides the binding sites n (from the slope) and the value of log[B] at log\((F_0 - F_x)/(F_x - F_{\text{end}})\) = 0 gives log(Kd).\(^{1}\)

Figure S8. Double-logarithmic plot for the spectral change of 2 (water, c = 5.8 \times 10^{-8} \text{ M}, \lambda_{ex} = 400 \text{ nm}) upon addition of Na\(_3\)PO\(_4\) (water, c = 11.6 \mu\text{M}).
Figure S9. Emission spectra of 2 (water, $c = 5.8 \times 10^{-8}$ M, $\lambda_{ex} = 400$ nm) upon addition of NaH$_2$PO$_4$ (water, $c = 11.6$ $\mu$M or 0.116 mM).

Most important for an efficient phosphate complexation is the pH value of the solution. A comparison of Na$_3$PO$_4$, Na$_2$HPO$_4$ and NaH$_2$PO$_4$ reveals clear differences (Figures 2, 3 and 4). Na$_3$PO$_4$ as well as Na$_2$HPO$_4$ possess the ability to complex Zn$^{II}$ and, therefore, enable a decomplexation of the Zn$^{II}$ terpyridine complex. In contrast, NaH$_2$PO$_4$ behaves like most of the other ions, just coordinates to Zn$^{II}$ and, consequently, does not shift the emission wavelength (Figure S9). This knowledge enables a clear distinction between the “alkaline” phosphates (Na$_3$PO$_4$ and Na$_2$HPO$_4$) as well as NaH$_2$PO$_4$ and, thereby, for a given phosphate concentration, estimation of the pH value.

Figure S10. Double-logarithmic plot for the spectral change of 2 (water, $c = 5.8 \times 10^{-8}$ M, $\lambda_{ex} = 400$ nm) upon addition of Na$_4$P$_2$O$_7$ (water, $c = 11.6$ $\mu$M).
Figure S11. Double-logarithmic plot for the spectral change of 2 (water, c = 5.8 × 10⁻⁸ M, λ<sub>ex</sub> = 400 nm) upon addition of KCN (water, c = 11.6 μM).

Table S1. Overview about the composition of tap water from Jena, Germany.<sup>3</sup>

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<sup>a</sup> Equivalents in comparison to concentration of 2 (5.8 × 10⁻⁸ M).

2. Personal message, Prof. Dr. Shin Mizukami (smizukami@mls.eng.osaka-u.ac.jp).