

## Supporting information for:

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

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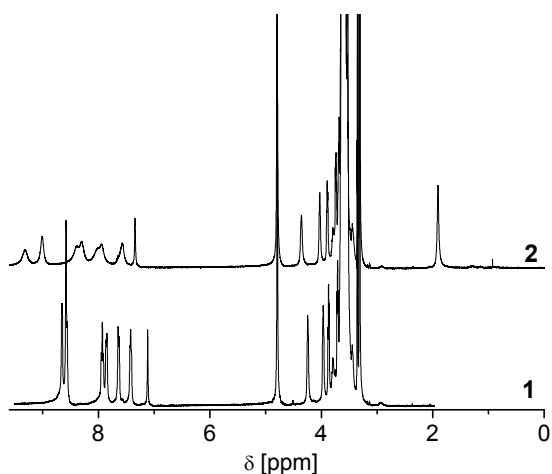


Figure S1. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz) of **1** and **2**.

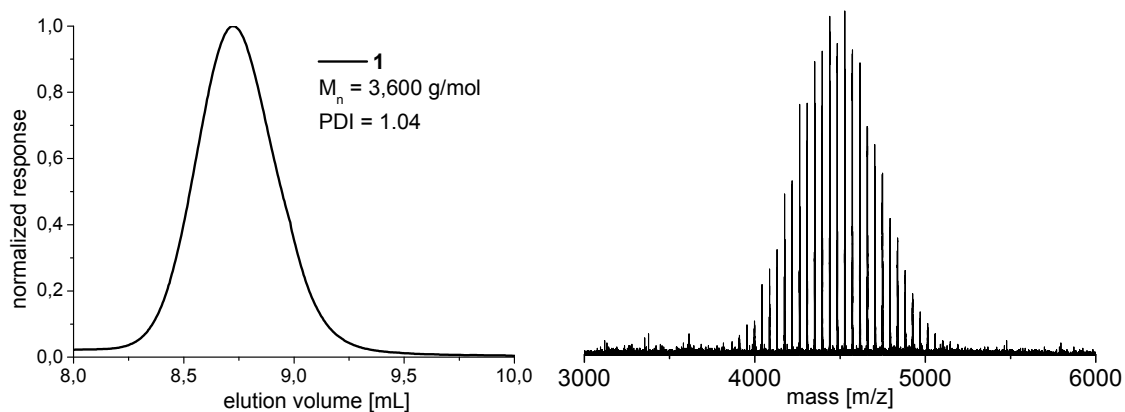


Figure S2. Left: SEC trace of **1**. Right: MALDI-TOF MS spectrum of **1**.

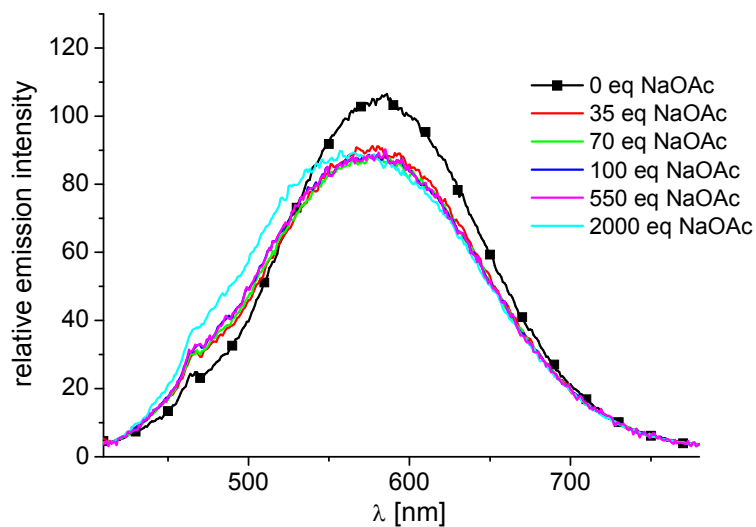


Figure S3. Emission spectra of **2** (water,  $c = 5.8 \times 10^{-8}$  M,  $\lambda_{\text{ex}} = 400$  nm) upon addition of NaOAc (water,  $c = 11.6 \mu\text{M}$  or  $0.116$  mM).

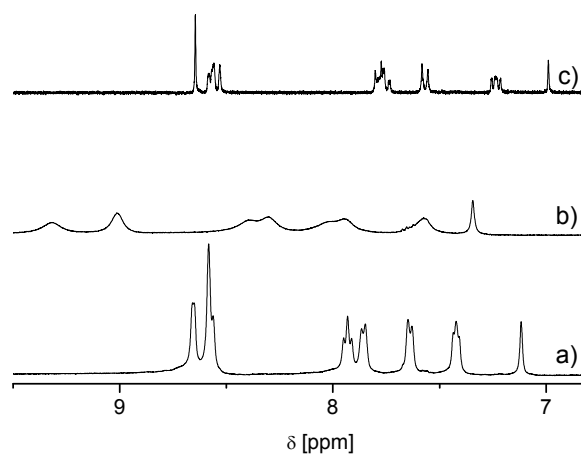


Figure S4.  $^1\text{H}$  NMR a) **1** ( $\text{CD}_3\text{OD}$ , 400 MHz), b) **2** ( $\text{CD}_3\text{OD}$ , 400 MHz), c) **2** upon addition of 50 equivalents  $\text{Na}_3\text{PO}_4$  ( $\text{D}_2\text{O}$ , 200 MHz).

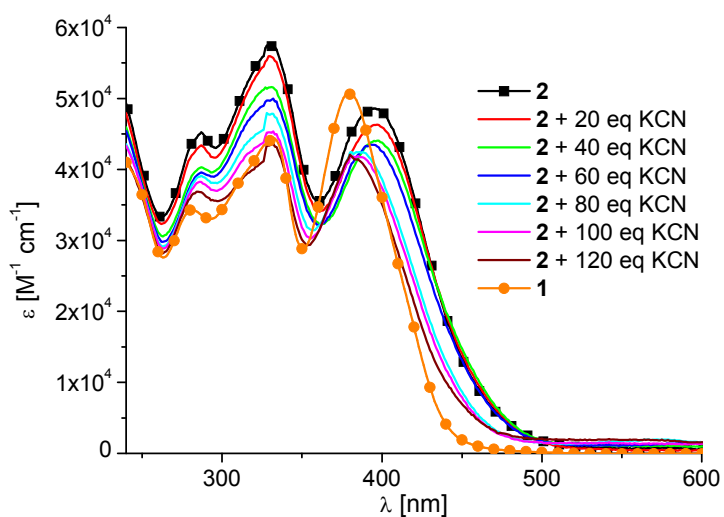


Figure S5. UV-Vis absorption spectra ( $10^{-6}$  M, water) of **1** and **2**, upon addition of KCN.

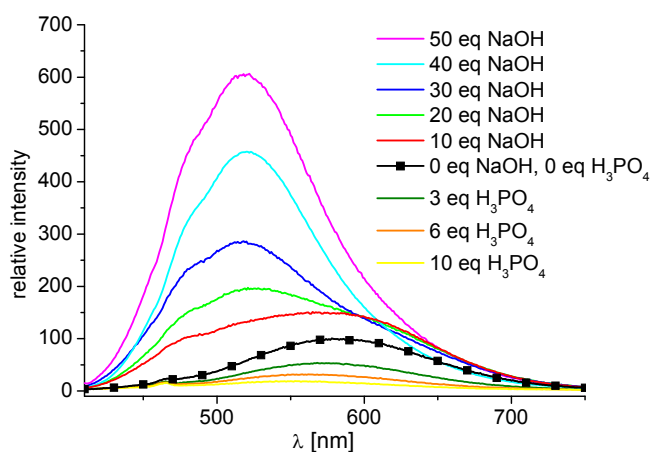


Figure S6. Emission spectra of **2** (water,  $c = 5.8 \times 10^{-8}$  M,  $\lambda_{\text{ex}} = 400$  nm) upon addition of NaOH or  $\text{H}_3\text{PO}_4$  (water,  $c = 11.6$   $\mu\text{M}$ ).

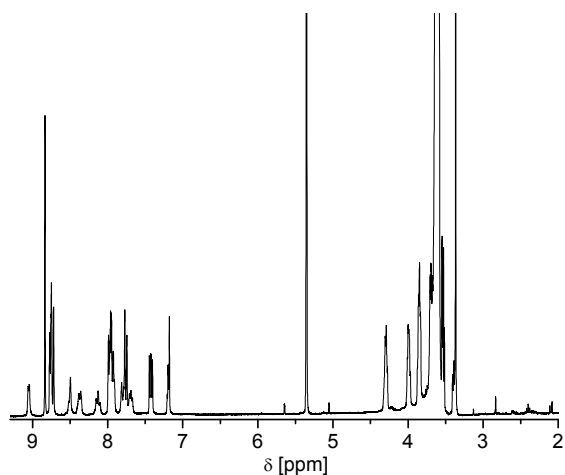
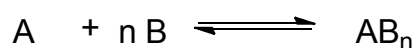


Figure S7.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz) of **2** upon addition of one equivalent NaOH.

### Calculation of the dissociation constants

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



$$K_d^n = \frac{[\text{A}][\text{B}]^n}{[\text{AB}_n]} \quad (\text{Eq. S1})$$

When  $[\text{A}]_0 = [\text{A}] + [\text{AB}_n]$  is the initial concentration of A and  $[\text{B}]_0$  the initial concentration of B.

Therefore:

$$K_d^n = \frac{([\text{A}]_0 - [\text{AB}_n])[\text{B}]^n}{[\text{AB}_n]} \quad \text{and} \quad [\text{AB}_n] = \frac{[\text{A}]_0[\text{B}]^n}{K_d^n + [\text{B}]^n} \quad (\text{Eq. S2})$$

If  $I_A$  and  $I_{\text{AB}_n}$  are the proportional constants for the fluorescence intensity:

$$F_0 = I_A[\text{A}]_0 \quad \text{and} \quad F_{\text{end}} = I_{\text{AB}_n}[\text{A}]_0$$

$$\begin{aligned}
 F_x &= I_A[A] + I_{AB_n}[AB_n] \\
 &= I_A([A_0] - [AB_n]) + I_{AB_n}[AB_n] \\
 &= I_A[A_0] + (I_{AB_n} - I_A)[AB_n] \\
 &= I_A[A_0] + (I_{AB_n} - I_A) \frac{[A_0][B]^n}{K_d^n + [B]^n} \\
 &= F_0 + \frac{(F_{end} - F_0)[B]^n}{K_d^n + [B]^n}
 \end{aligned}
 \tag{Eq. S3}$$

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

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

The plot of  $\log\left\{\frac{F_0 - F_x}{F_x - F_{end}}\right\}$  vs.  $\log[B]$  provides the binding sites  $n$  (from the slope) and the value of  $\log[B]$  at  $\log\left\{\frac{F_0 - F_x}{F_x - F_{end}}\right\} = 0$  gives  $\log(K_d)$ .<sup>1</sup>

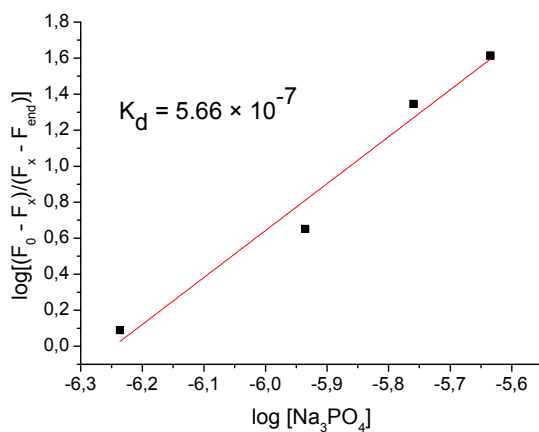


Figure S8. Double-logarithmic plot for the spectral change of **2** (water,  $c = 5.8 \times 10^{-8}$  M,  $\lambda_{ex} = 400$  nm) upon addition of Na<sub>3</sub>PO<sub>4</sub> (water,  $c = 11.6$  μM).

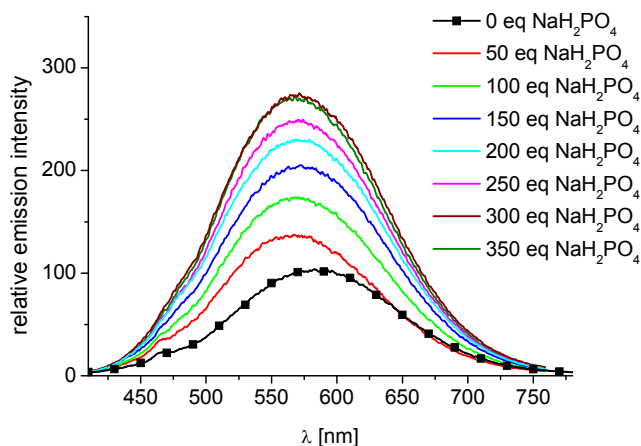


Figure S9. Emission spectra of **2** (water,  $c = 5.8 \times 10^{-8}$  M,  $\lambda_{\text{ex}} = 400$  nm) upon addition of  $\text{NaH}_2\text{PO}_4$  (water,  $c = 11.6 \mu\text{M}$  or  $0.116$  mM).

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

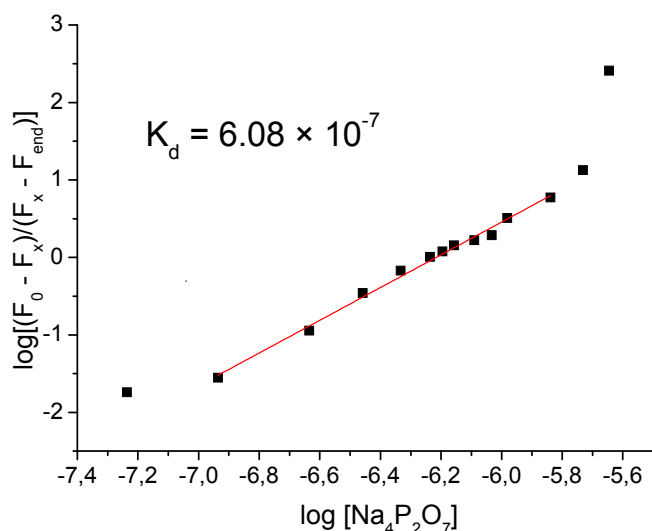


Figure S10. Double-logarithmic plot for the spectral change of **2** (water,  $c = 5.8 \times 10^{-8}$  M,  $\lambda_{\text{ex}} = 400$  nm) upon addition of  $\text{Na}_4\text{P}_2\text{O}_7$  (water,  $c = 11.6 \mu\text{M}$ ).

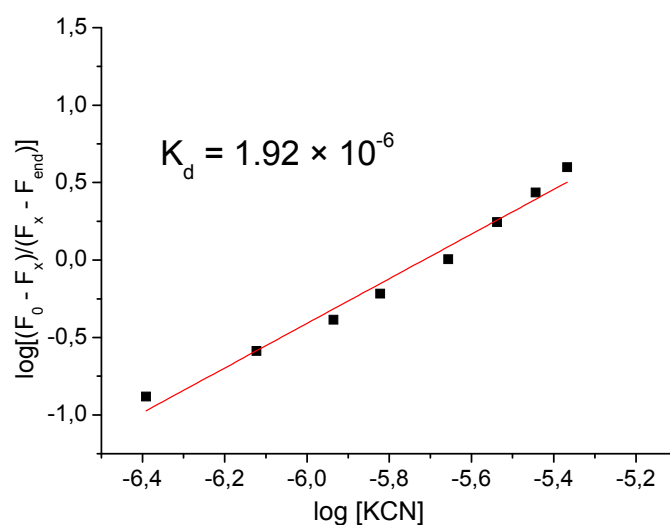


Figure S11. Double-logarithmic plot for the spectral change of **2** (water,  $c = 5.8 \times 10^{-8}$  M,  $\lambda_{\text{ex}} = 400$  nm) upon addition of KCN (water,  $c = 11.6$   $\mu\text{M}$ ).

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

	c	c	equivalents <sup>a</sup>
	[mg/l]	[M]	
phosphate	0.1	$1.0 \times 10^{-6}$	17
chloride	15.3	$4.4 \times 10^{-4}$	7586
nitrite	0.002	$4.3 \times 10^{-8}$	1
nitrate	5.28	$8.5 \times 10^{-5}$	1466
ammonium	<0.02	$<1.1 \times 10^{-6}$	<19
fluoride	0.11	$5.8 \times 10^{-6}$	100
iron	0.01	$1.7 \times 10^{-7}$	3
manganese	<0.01	$<1.8 \times 10^{-7}$	3
potassium	4.55	$1.8 \times 10^{-4}$	3100
sodium	10.9	$4.7 \times 10^{-4}$	8103
uranium	0.0061	$2.6 \times 10^{-8}$	0.45

a) Equivalents in comparison to concentration of **2** ( $5.8 \times 10^{-8}$  M).

1. P. Das, A. Ghosh, M. K. Kesharwani, V. Ramu, B. Ganguly and A. Das, *Eur. J. Inorg. Chem.*, 2011, 3050-3058.
2. Personal message, Prof. Dr. Shin Mizukami (smizukami@mls.eng.osaka-u.ac.jp).
3. <http://www.jenawasser.de/PDF/TWAnalyseBurgau.pdf> (25. 01. 2012).