Supporting Information

Metal-Cation Recognition in Water by a Tetrapyrazinoporphyrine-Based Tweezer Receptor


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Content:

Methods used for photophysical studies ................................................................. S1
Dependences of $\Phi_F$ of target sensors on the concentration of added analyte .......... S3
The effect of water in THF solution ........................................................................ S5
Fluorescence titration experiments in water ........................................................... S5
Competition experiments ....................................................................................... S6
Characterization of silica nanoparticles ................................................................. S7
NMR spectra ......................................................................................................... S8
References ........................................................................................................... S13
Methods used for photophysical studies

**Fluorescence measurements**

Fluorescence quantum yields (ΦF) were determined by the comparative method using unsubstituted ZnPc (ΦF = 0.32 in THF[1]). Samples were excited at 595 nm. ΦF was calculated using Equation (Eq. 1) where F is the integrated area under the emission spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the solvent. The superscripts R and S correspond to the reference and sample, respectively. Estimated error ± 15%.

$$\Phi_F^S = \Phi_F^R \left( \frac{F^S}{F^R} \right) \left( \frac{1}{1 - 10^{-A^S}} \right) \left( \frac{n^S}{n^R} \right)^2$$  

(Eq. 1)

**Determination of binding constant**

A dye stock solution in THF (15 - 20 µL) was added to a 10 × 10 mm fluorescence quartz cell with 2.5 mL of THF (HPLC, <0.05% H2O) to reach a final concentration of 1 µM. The absorption and emission spectra (λexc = 595 nm) were recorded. Then, defined amounts (typically 10 - 100 µL) of a stock solution (typically 0.01 M, 0.1 M or 1 M) containing the analyte in the form of a perchlorate (in the case of Li+, Na+, Mg2+, Ca2+, and Ba2+) or thiocyanate (in the case of K+) salt in MeOH (<0.03 % H2O) were added. The absorption and emission spectra were recorded after each addition, and the fluorescence quantum yields were determined for each point. The fluorescence quantum yields were calculated as mentioned above and plotted as a function of the analyte concentration. Association constants (K-values) were calculated by non-linear regression analysis using the Prism 5 software for Windows (GraphPad Software, Inc.). In the cases of biphasic titration curves, the first part of the titration curves was analysed separately.

**Fluorescence enhancement factor**

The fluorescence enhancement factor (FEF) was calculated as follows: FEF = ΦF(M⁺) / ΦF(Free), where ΦF(Free) is ΦF in THF (1 µM) before the addition of any analyte, ΦF(M⁺) is ΦF at complete saturation of the analyte in the cavity of the recognition moiety (i.e., when the titration curve from the “Determination of binding constant” reached an apparent plateau). In the cases of biphasic titration isotherms, FEF1 corresponds to the increase of fluorescence intensity of the first step, total FEF corresponds to the increase of fluorescence intensity for both steps together.

**Fluorescence titration experiments of 1bZn@NP**

A total of 2.5 mL of a 1bZn@NP (c ~ 1 µM) stock solution in water/acetic acid = 3:1 (v/v) was transferred to a 10 × 10 mm fluorescence quartz cell, and absorption and emission spectra (λexc = 599 nm) were recorded. Then, defined amounts (typically 5-50 µL) of stock solution (1 M) of analyte in H2O/acetic acid = 3:1 (v/v) were subsequently added and absorption and emission spectra were measured after each addition. The fluorescence intensity was corrected to the same absorption at the excitation wavelength and plotted as a function of the analyte concentration.

**Job’s method of continuous variation**

Stock solutions of 1bZn (100 µM) in THF and of 1 mM for KSCN in MeOH were prepared. A series of fluorescence measurements with different 1bZn/KSCN (13 or 15 measurements ranging between 1:5 to 5:1 ratios) were performed as follows: an appropriate amount of THF that resulted in a the total volume of the solution being 1.00 mL after the addition of stock solutions of 1bZn and analyte was transferred to a 10 × 4 mm fluorescence quartz optical cell. A stock solution containing 1bZn was added, and the fluorescence emission spectrum was recorded (λexc = 595 nm). The fluorescence intensity at maximum was considered to be F0. An appropriate amount of analyte stock solution was added to yield a total concentration of components of 10 µM ([1bZn] + [K⁺] = 10 µM). The fluorescence emission spectrum was recorded and Fmax was found as the fluorescence intensity at maximum. The final stoichiometry of the 1bZn/K⁺ complex was determined from the Job’s plot constructed from the dependence of Fmax/F0 on [K⁺]/([K⁺]+[1bZn]).
Dependences of $\Phi_F$ of target sensors on the concentration of added analyte

Fig. S1. Fluorescence titration experiments of 1aZn in THF ($C_{(TPyPz)} = 1 \mu$M) by Li$^+$ (a), Na$^+$ (b), K$^+$ (c), Mg$^{2+}$ (d), Ca$^{2+}$ (e), Ba$^{2+}$ (f) in MeOH.

Fig. S2. Fluorescence titration experiments of 1bZn in THF ($C_{(TPyPz)} = 1 \mu$M) by Li$^+$ (a), Na$^+$ (b), K$^+$ (c), Mg$^{2+}$ (d), Ca$^{2+}$ (e), Ba$^{2+}$ (f) in MeOH.
Fig. S3. Fluorescence titration experiments of 1cZn in THF (cTPyPz = 1 μM) by Li⁺ (a), Na⁺ (b), K⁺ (c), Mg²⁺ (d), Ca²⁺ (e), Ba²⁺ (f) in MeOH.
The effect of water in THF solution

Fig. S4. Fluorescence titration experiments with water. Original solutions consisted of 1bZn in anhydrous THF (c_{TPyPz} = 1 μM) and K⁺ (a), Ca²⁺ (b) and Ba²⁺ (c) (dissolved in anhydrous MeOH) at their complete binding.

Fluorescence titration experiments in water

Fig. S5. Titration of 1bZn@NP in water/acetic acid 3:1 (c_{TPyPz} = 1 μM) with K⁺ (a), Ca²⁺ (b) and Ba²⁺ (c). Fluorescence intensity was corrected for changes of absorbance at excitation wavelength.

Fig. S6. Changes in absorption spectra of 1bZn@NP upon titration with K⁺ (concentration of K⁺ ranges from 0 to 220 mM).
Competition experiments

**Fig. S7.** Fluorescence titration experiment of 1bZn in THF (c_{TPyPz} = 1 μM) titrated with KSCN (in MeOH) in the presence of 5 mM Na⁺.

**Fig. S8.** Titration of 1bZn@NP in water/acetic acid 3:1 (c_{TPyPz} = 1 μM) with K⁺ (a) in the presence of Na⁺ (5 mM) (a) or Ca²⁺ (2 mM) (b). Enlarged areas of graphs show the negligible increase of fluorescence after addition of competitive cations.
Characterization of silica nanoparticles

The size of particles in water was determined on a particle size analyzer Zetasizer Nano ZS from Malvern (United Kingdom). In addition, nanoparticles were also investigated by high-resolution transmission electron microscopy (HRTEM) using a JEM-3010 (JEOL, Japan) operating at 300 kV in conjunction with an EDX detector (Oxford Instruments, United Kingdom).

![Size Distribution of 1bZn@NP Silica Nanoparticles](image)

**Fig. S9.** Size distribution of 1bZn@NP silica nanoparticles in water dispersions at room temperature.

![HRTEM Images of 1bZn@NP Silica Nanoparticles](image)

**Fig. S10.** HRTEM images of 1bZn@NP silica nanoparticles.
Fig. S11. $^1$H NMR spectrum of 3a in acetone-$d_6$. Asterisks indicate residuals of non-deuterated solvent (acetone), triangle indicates water.

Fig. S12. $^1$H NMR spectrum of 3b in CDCl$_3$. Asterisk indicates residuals of non-deuterated solvent.
Fig. S13. $^1$H NMR spectrum of 3c in acetone-d$_6$. Asterisk indicates residuals of non-deuterated solvent, triangle indicates water.

Fig. S14. $^1$H NMR spectrum of 1aH in CDCl$_3$/pyridine-d$_5$. Asterisks indicate residuals of non-deuterated solvent, triangle indicates water.
Fig. S15. $^1$H NMR spectrum of 1bH in CDCl$_3$/pyridine-$d_5$. Asterisk indicates residuals of non-deuterated solvent, triangle indicates water.

Fig. S16. $^1$H NMR spectrum of 1cH in CDCl$_3$/pyridine-$d_5$. Asterisk indicates residuals of non-deuterated solvent, triangle indicates water.
Fig. S17. $^1$H NMR spectrum of 1aZn in CDC$_3$/pyridine-$d_5$. Asterisks indicate residuals of non-deuterated solvents, triangle indicates water.

Fig. S18. $^1$H NMR spectrum of 1bZn in CDC$_3$/pyridine-$d_5$. Asterisks indicate residuals of non-deuterated solvents, triangle indicates water.
Fig. S19. $^1$H NMR spectrum of 1cZn in CDCls/pyridine-d$_5$. Asterisks indicate residuals of non-deuterated solvents, triangle indicates water.
References