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A novel fluorescent indicator for Ba^{2+} in aqueous micellar solutions†

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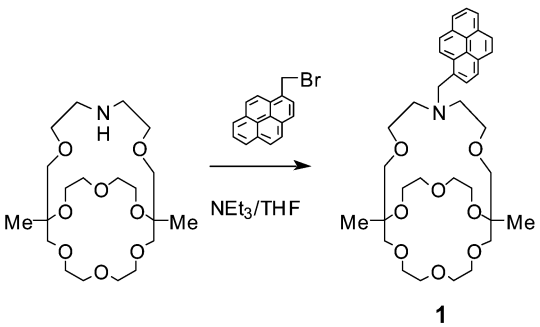
The highly selective and sensitive fluorescence detection of Ba^{2+} among alkali metal and alkaline earth metal cations was successfully achieved in aqueous media by the combination of a novel monoazacryptand type of fluorophore and micelles of Triton X-100.

Since the fluorescent detection of metal ions using fluorophores is one of the best methods to discriminate with high sensitivity between metal cations, including alkali metal and alkaline earth metal cations, much effort has been devoted to the design and development of new types of fluorophores exhibiting high selectivity in addition to high sensitivity. Crown ethers and their analogous compounds are specific hosts for alkali metal and alkaline earth metal cations, and are functionalised by the introduction of fluorescent substituents.[1] These hosts are effective as selective fluorophores in organic media, but most of them lose their specificity in aqueous media because their complexing abilities are drastically decreased by strong hydration.[2] For example, lariat ether-type fluorophores with a pyrene moiety at each end of their two sidearms can selectively detect alkaline earth metal cations in acetonitrile[3] by using the effective coordination of one of the electron-donating sidearms, but become ineffective in aqueous solution. This result indicates that much stronger complexing ability is required for the fluorophore when used in aqueous media. Thus, the number of fluorophores effective in aqueous media has been rather limited,[4] and it is still desirable to propose a new concept for the design of a fluorescence detection system for a specific metal cation. Our strategy for this design is based on the use of a cryptand scaffold together with the use of the less polar region of aqueous micelles[5] as a field for cation complexation. From this viewpoint, we describe the design and synthesis of a novel type of fluorophore, monoazacryptand **1**, and examine its fluorescence properties in both aqueous and micelle solutions.

Pyrene-functionalised monoazacryptand **1** was prepared by the *N*-alkylation of the corresponding monoazacryptand[6] with 1-pyrenylmethyl bromide in THF in the presence of triethylamine (Scheme 1).[7] The structure was ascertained by ^{1}H-NMR and IR spectroscopy, mass spectrometry, and elemental analysis.‡

The fluorescence of monoazacryptand **1** based on its pyrene ring is quenched due to the photoinduced electron transfer (PET)[8] from the amino group in the free state. Upon complexation with a metal cation, the nitrogen lone pair no longer participates in PET, causing the recovery of the fluorescence. Therefore, this mechanism results in an intensity-based sensor governed by ion binding in this study.



Scheme 1

At first, we measured the fluorescence spectra of **1** in aqueous solution as a function of the concentration of $Ba(SCN)_2$ in aqueous solution (**1** = 1.0×10^{-6} M, Tris = 1.0×10^{-2} M, pH = 10.2) to evaluate the complexation behavior of cryptand **1**. In this case, the addition of a large excess of Ba^{2+} to **1** only slightly changed the fluorescence intensity (Fig. 1a). This result clearly indicates that the complexing ability of **1** toward Ba^{2+} is insufficient for its fluorescent detection in aqueous solution. In order to improve the complexing ability of **1**, we added Triton X-100 surfactant micelles into the aqueous solution. Our hypothesis was that the solubilization of **1** into these micelles would make possible the complexation of **1** with Ba^{2+} in the less polar region, leading to an enhancement of the Ba^{2+} complexing ability of **1**.

The fluorescence spectral changes of **1** in the presence of Triton X-100 surfactant micelles are shown in Fig. 1b. The addition of Ba^{2+} remarkably affected the fluorescence intensity of **1**, in agreement with our expectation. It should be noted that the addition of only a small excess of Ba^{2+} to the ligand dramatically increased the fluorescence intensity of **1**. When Ba^{2+} is added, the amino nitrogen atom becomes involved in complexing with Ba^{2+} and loses its ability to donate an electron to the excited state of the pyrene ring. Thus, the addition of Ba^{2+} caused the recovery of the fluorescence.

To clarify the micelle effect of Triton X-100, the ratio of the fluorescence intensity in the presence of Ba^{2+} ($I_{complex}$) to that in the absence of Ba^{2+} (I_{free}) was plotted against the concentration of Triton X-100 (Fig. 2). Fig. 2 shows that the recovery of the fluorescence intensity began when the concentration of Triton X-100 reached the critical micellar concentration level (0.24 mM).[9] This suggests that **1** is incorporated into the micelle and as a result the hydrophobic environment promotes the complexation of **1** to Ba^{2+}.

The selectivity towards other cations was examined next (Fig. 3). The thiocyanate salts of alkali metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+) and alkaline earth metal cations (Mg^{2+}, Ca^{2+}, Ba^{2+}) were used to evaluate the binding ability. Surprisingly, **1** displayed a large

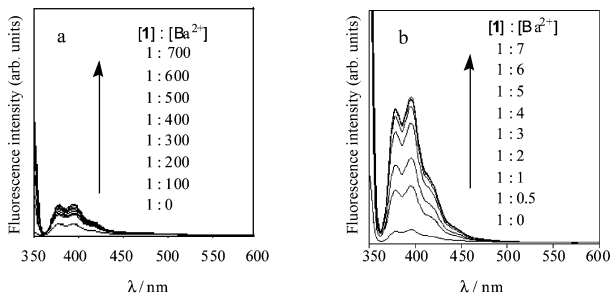


Fig. 1 Fluorescence spectral changes of **1** (1×10^{-6} M) with different concentrations of Ba^{2+} in water containing Tris (1×10^{-2} M, pH = 10.2) in the absence (a) of and presence (b) of Triton X-100 (5×10^{-3} M); Excitation wavelength : 342 nm.

† Electronic supplementary information (ESI) available: synthesis and characterisation of **1**. See http://www.rsc.org/suppdata/cc/b3/b311613a/

DOI: 10.1039/b311613a

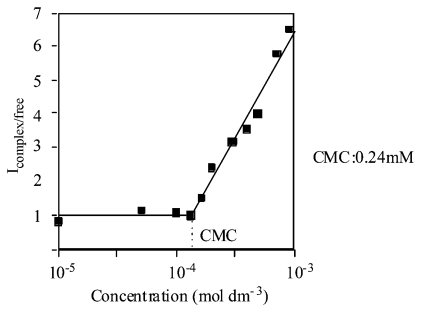


Fig. 2 Changes in the $I_{complex}/I_{free}$ of **1** (1×10^{-6} M) with different concentrations of Triton X-100 in water containing Ba^{2+} (5 equiv., 5×10^{-6} M) and Tris (1×10^{-2} M, pH = 10.2); Excitation wavelength: 342 nm.

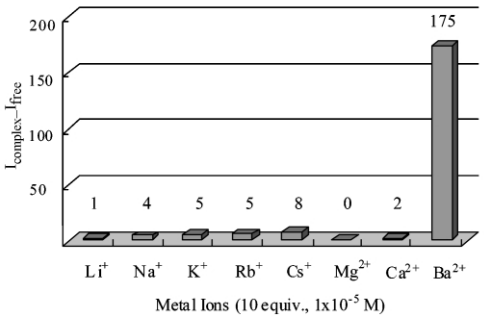


Fig. 3 CHEF effects of **1** (1×10^{-6} M) with metal ions in water in the presence of Triton X-100 (5×10^{-3} M) containing Tris (1×10^{-2} M, pH = 10.2); Excitation wavelength: 342 nm.

chelation-enhancement fluorescence (CHEF)[10] with only Ba^{2+} among these metal ions. The experimental data ($I_{complex}$-I_{free}) demonstrated that **1** is a highly sensitive and selective sensor for Ba^{2+} in aqueous solution. When the corresponding monoaza-18-crown-6 ether derivative[7] was used as a fluorophore instead of **1**, the addition of metal cations (1mM, 1000 equiv.) barely changed the fluorescence behavior, even in the presence of the Triton X-100 micelles. This result clearly demonstrates that the strong complexing ability of the cryptand scaffold is requisite for the detection of metal ions, even in micellar solutions.

In conclusion, we have developed a new fluorescent detection device for Ba^{2+} in aqueous media by combining a pyrene-functionalised monoazacryptand **1** exhibiting high selectivity and sensitivity towards Ba^{2+} with micelles formed by a non-ionic surfactant (Triton X-100). The molecular design of fluorophores effective for the detection of other metal cations is now in progress. We believe that a variety of fluorophores can be effectively used in micellar solutions in the future.

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Notes and references

‡ Spectroscopic data for **1**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 6H), 2.87–2.98 (m, 4H), 3.48–3.85 (m, 28H), 4.33 (s, 2H), 7.95–8.56 (m, 9H). IR (neat, cm^{-1}) *v*: 3040, 2820, 1930, 1740, 1590, 1450, 1370, 1300, 1040, 850, 710. MS (FAB) (*m*/*z*) 636 ($M^+ + 1$). Anal. Calcd for $C_{37}H_{49}O_8N_1$: C, 69.90; H, 7.77; N, 2.20. Found: C, 69.96; H, 7.79; N, 1.91.

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