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Fluorometric sensing of alkali metal and alkaline earth metal cations by novel photosensitive monoazacryptand derivatives in aqueous micellar solutions

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Novel monoazacryptand-type fluorescent chemosensors, **1** (derived from an 18-crown-6) and **2** (derived from a 15-crown-5) both with a pyrene ring as their photoresponsive moiety, were synthesized. Their fluorescence properties for alkali metal and alkaline earth metal cations in water were then examined. The detection of metal cations was accomplished by a change in the fluorescence intensity of the host compounds, based on a photoinduced electron transfer (PET) mechanism. In aqueous solution, **1** showed little fluorescence upon the addition of Ba^{2+} because of the very weak complexation with Ba^{2+}, but the presence of micelles of polyoxyethylene(10) isooctylphenyl ether (Triton X-100) enabled **1** to show highly sensitive and selective Ba^{2+} detection among alkali metal and alkaline earth metal cations. With respect to the selective fluorescent detection of important metal cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) relevant to living organisms, **2** was found to detect K^+ with high selectivity in aqueous micellar solutions of polyoxyethylene(20) sorbitan monostearate (Tween-60). The selectivity for metal cations was mainly dependent on the goodness of fit of the host cavity and the metal cation size. In the presence of anionic surfactants, **2** detected alkaline earth metal cations more effectively than alkali metal cations.

Introduction

The design of chemosensors, molecules that can selectively recognize the presence of a specific analyte, is an important goal of supramolecular chemistry.[1] Since the fluorescent detection of metal ions using fluorophores is one of the most powerful methods to discriminate 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 can be functionalised by the introduction of fluorescent substituents.[2] These hosts are effective as selective fluorophores in organic media, but most of them lose their specificity in aqueous media because their complexation abilities are drastically decreased by strong hydration.[3] 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[4] using the effective coordination of one of their electron-donating sidearms, but become ineffective in aqueous solutions. This result indicates that much stronger complexation ability is required for the fluorophore when used in aqueous media. Thus, the number of fluorophores effective in aqueous media has been rather limited,[5] and it remains a challenge to design a new fluorescence detection system for a specific metal cation in water. Cryptands are well known to be very effective host molecules for alkali metal and alkaline earth metal cations because of their highly preorganized three-dimensional structures.[6] Our strategy for this design is based on the use of a cryptand scaffold, together with the use of the less polar regions of aqueous micelles[7] as complexation fields for cations. We recently achieved the highly selective and sensitive fluorescence detection of Ba^{2+} among alkali metal and alkaline earth metal cations in aqueous media by the combination of a monoazacryptand type of fluorophore and the Triton X-100 micelles.[8] Based on this knowledge, in this study, we describe the design and synthesis of novel monoazacryptand-type fluorophores and their fluorescence properties for alkali metal and alkaline earth metal cations were examined in water in the presence of nonionic surfactants such as Triton X-100, polyoxyethylene(20) sorbitan monolaurate (Tween-20), polyoxyethylene(20) sorbitan monostearate (Tween-60), polyoxyethylene(20) stearyl ether (Brij-78), *n*-dodecyl-β-maltopyranoside, and poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer (Pluronic F-127), and ionic surfactants such as sodium dodecyl sulfate (SDS), sodium *n*-dodecylbenzenesulfonate (SDBS), sodium cholate (NaC), sodium deoxycholate (NaDC), tetramethylammonium dodecyl sulfate (TMADS), tetramethylammonium dodecanoate (TMADC), and cetyltrimethylammonium bromide (CTAB) (Fig. 1).

Results and discussion

Synthesis

Pyrene-functionalised monoazacryptands **1** and **2** were synthesized according to the procedure summarized in Scheme 1. The starting materials **5a** and **5b** were prepared according to a previous report.[9] The compounds **6a** and **6b** were prepared by the reaction of *cis*-2,12-bis(bromomethyl)-2,12-dimethyl-18-crown-6 and *cis*-2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5 with diethanolamine, respectively under basic conditions.[10] Fluorophores **1** and **2** were prepared by the *N*-alkylation of the corresponding monoazacryptand with 1-pyrenylmethyl bromide in THF in the presence of triethylamine.[11] Pyrene-functionalised monoazacrown ethers **3** and **4** were also prepared from the corresponding azacrown ethers[12] by the same method as **1** and **2**. All structures were confirmed by ^{1}H-NMR and IR spectroscopy, mass spectrometry, and elemental analysis.

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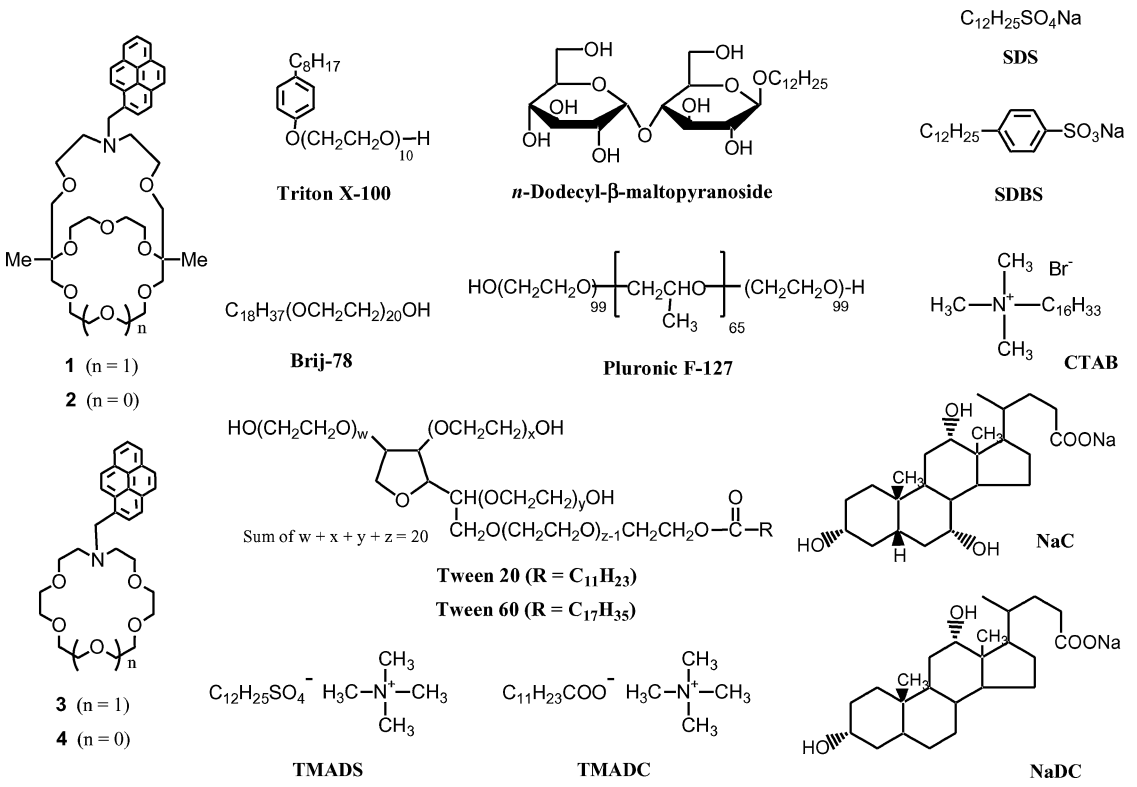
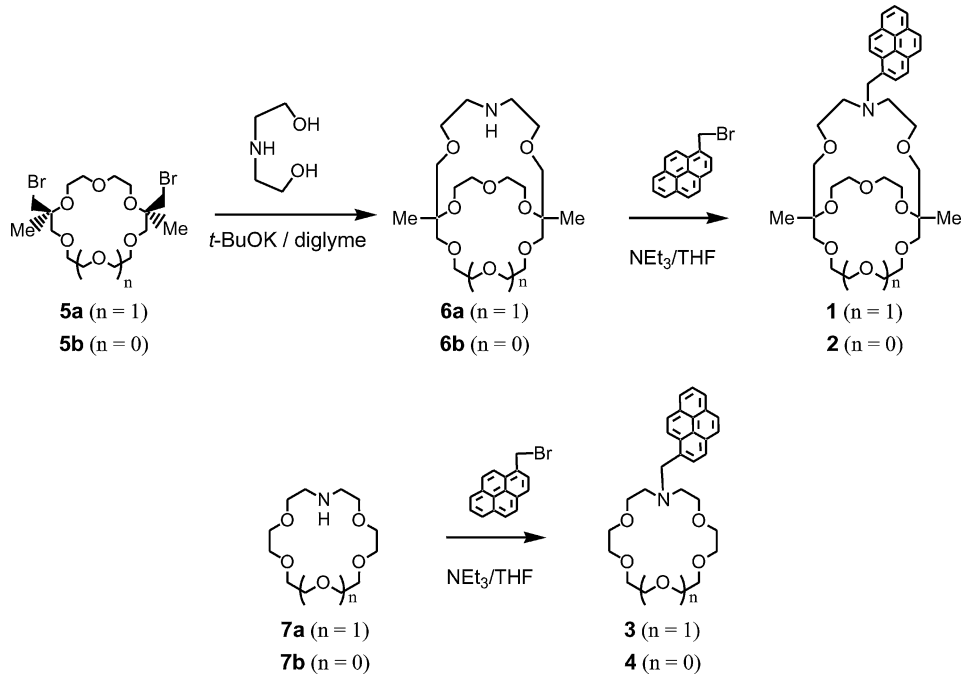


Fig. 1 Structures of fluorophores and surfactants.



Scheme 1 Synthesis of fluorophores **1**–**4**.

A fluorescent indicator for Ba^{2+} in aqueous micellar solutions[13]

Photoinduced electron transfer (PET)[14] types of fluorophores have proven to be highly successful as direct fluorescent cation sensing molecules.[15] The fluorescence of monoazacryptands is based on its pyrene ring, and is quenched due to PET from the amino nitrogen atom in the free state. Upon complexation with a metal cation, the nitrogen lone pair no longer participates in PET, causing a recovery of the fluorescence. The degree of fluorescence recovery upon the addition of metal cations is dependent on the complexation ability of the host compounds. Therefore, this results in a fluorescence intensity-based sensor governed by ion binding.

At first, we measured the fluorescence spectra of **1** in Tris solutions as a function of the concentration of $Ba(SCN)_2$ in order to evaluate its complexation behavior. In this case, the addition of a large excess of Ba^{2+} to **1** only slightly changed the fluorescence intensity (Fig. 2a). This result clearly indicates that the complexation ability of **1** toward Ba^{2+} is insufficient for its fluorescent detection in aqueous solution. In order to improve the complexation 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 enable the complexation of **1** with Ba^{2+} in the less polar regions.

The fluorescence spectral changes of **1** in the presence of Triton X-100 surfactant micelles are shown in Fig. 2b. The

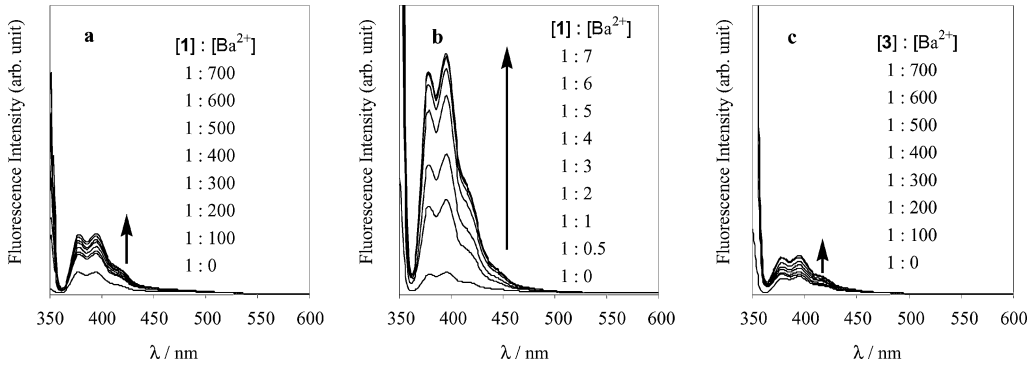


Fig. 2 Fluorescence spectral changes of **1** (1.0×10^{-6} M) and **3** (1.0×10^{-6} M) with different concentrations of $Ba(SCN)_2$ in Tris solutions (1.0×10^{-2} M Tris, pH = 10.2) in the absence (a) and presence (b), (c) of Triton X-100 (5.0×10^{-3} M). Excitation wavelength: 342 nm.

addition of Ba^{2+} remarkably affected the fluorescence intensity of **1**, in agreement with our expectations. 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 the complexation 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 a recovery of the fluorescence. When the corresponding monoaza-18-crown-6 ether derivative (**3**)[11] was used as a fluorophore instead of **1**, the addition of a large amount of Ba^{2+} barely changed the fluorescence behavior in the presence of the Triton X-100 micelles (Fig. 2c). This result clearly demonstrates that the strong complexation ability of the cryptand scaffold is necessary for the detection of metal ions, even in aqueous micellar solutions.

The stability constants (K) of the complexes were evaluated from a curve of the fluorescent intensity plotted against the ratio of [Ba^{2+}]/[Host] by means of a nonlinear least-squares curve-fitting method.[16] The K values of **1, 2**, and **3** towards Ba^{2+} in CH_3OH–CH_3CN (99 : 1 v/v), aqueous micellar solutions of Triton X-100, and H_2O–CH_3CN (99 : 1 v/v) are summarized in Table 1. These results show that the polar environment around the host compounds in the Triton X-100 micelles is intermediate between methanol and water.

To clarify the effects of the Triton X-100 surfactant micelles, the fluorescence intensity of **1** in the presence of Ba^{2+} (5.0×10^{-6} M, 5 equiv.) was plotted against the Triton X-100 concentration (Fig. 3). Fig. 3 shows that the recovery of the fluorescence intensity began when the Triton X-100 concentration reached the critical micellar concentration (0.24 mM).[17] Furthermore, it was shown that the fluorescence linearly increased with an increase in the Triton X-100 concentration above the cmc. This result supports our assumption that **1** is incorporated into the micelle, and that the hydrophobic environment of the micelle promotes the complexation ability of **1** with Ba^{2+}.

The selectivity towards other cations was also examined (Fig. 4). The thiocyanate salts of alkali metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+) and the perchlorate salts of alkaline earth metal cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) were used to evaluate the binding ability. Surprisingly, **1** displayed a large chelation-enhanced fluorescence (CHEF) effect ($I_{complex} - I_{free}$),[18] where I_{free} and $I_{complex}$ are the fluorescence intensities (monitored at 394 nm) in the

Table 1 Stability constants (log K) of **1, 2**, and **3** for Ba^{2+} in CH_3OH–CH_3CN (99 : 1 v/v), aqueous micellar solutions of Triton X-100, and H_2O–CH_3CN (99 : 1 v/v)

	log K (M^{-1})		
	CH_3OH	Aqueous micellar solutions of Triton X-100	H_2O
1	9.7	6.6	3.4
2	6.1	4.7	n.d.
3	4.9	n.d.	n.d.

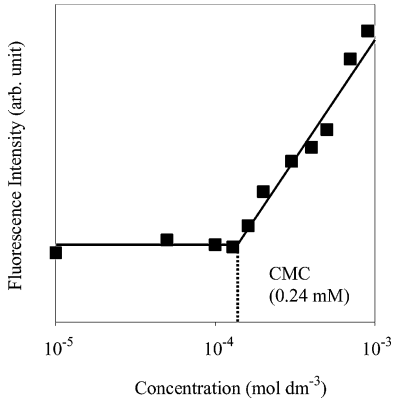


Fig. 3 Changes of the fluorescence intensity of **1** (1.0×10^{-6} M) with different concentrations of Triton X-100 in Tris solutions (1.0×10^{-2} M Tris, pH = 10.2) containing $Ba(SCN)_2$ (5.0×10^{-6} M, 5 equiv.). Excitation wavelength: 342 nm.

absence and presence of metal cations (1.0×10^{-5} M, 10 equiv.), respectively, with only Ba^{2+} among these metal cations. Fig. 4 demonstrates that **1** (derived from 18-crown-6) is a highly sensitive and selective sensor for Ba^{2+} in water. Indeed, the response of fluorophore **1** towards Ba^{2+} was barely affected, even in the presence of a large excess of other alkali metal and alkaline earth metal cations. On the other hand, in the case of **2** (derived from 15-crown-5), the addition of all alkali metal and alkaline earth metal cations barely caused any CHEF effects. This demonstrated that the stronger complexation ability based on the 18-crown-6 ring was necessary for the highly sensitive detection of Ba^{2+}.

Selective fluorescent detection of important metal cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) relevant to living organisms in aqueous micellar solutions

Next, the selective fluorescent detection of important metal cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) relevant to living organisms using fluorophores was carried out. Selective fluorescent discrimination among these metal cations in water is required in fields such as clinical diagnosis and environmental analysis. Therefore, the fluorescent properties of photosensitive monoazacryptands for these metal cations were examined in aqueous micellar solutions of nonionic surfactants such as Triton X-100, Tween-20, Tween-60, Brij-78, *n*-dodecyl-β-maltopyranoside, and Pluronic F-127 and ionic surfactants such as SDS, SDBS, NaC, NaDC, TMADS, TMADC, and CTAB. Here, the chloride salts of alkali metal (Na^+, K^+) and alkaline earth metal (Mg^{2+}, Ca^{2+}) cations (1.0×10^{-3} M, 1000 equiv.) were used in consideration of practical analysis.

Fig. 5 shows the CHEF effects upon the addition of metal cations in the presence of various nonionic surfactants. Among these nonionic surfactants, in the presence of Tween-60,

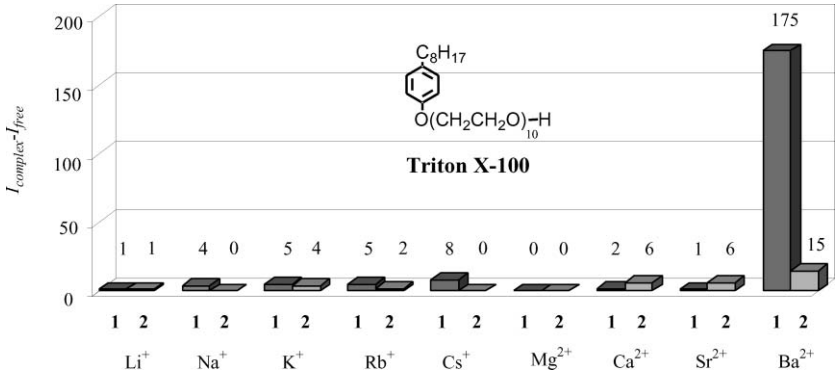


Fig. 4 CHEF effects of **1** (1.0×10^{-6} M) and **2** (1.0×10^{-6} M) with thiocyanate salts (1.0×10^{-5} M, 10 equiv.) of alkali metal and alkaline earth metal cations in Tris solutions (1.0×10^{-2} M Tris, pH = 10.2) in the presence of Triton X-100 (5.0×10^{-3} M). Excitation wavelength: 342 nm.

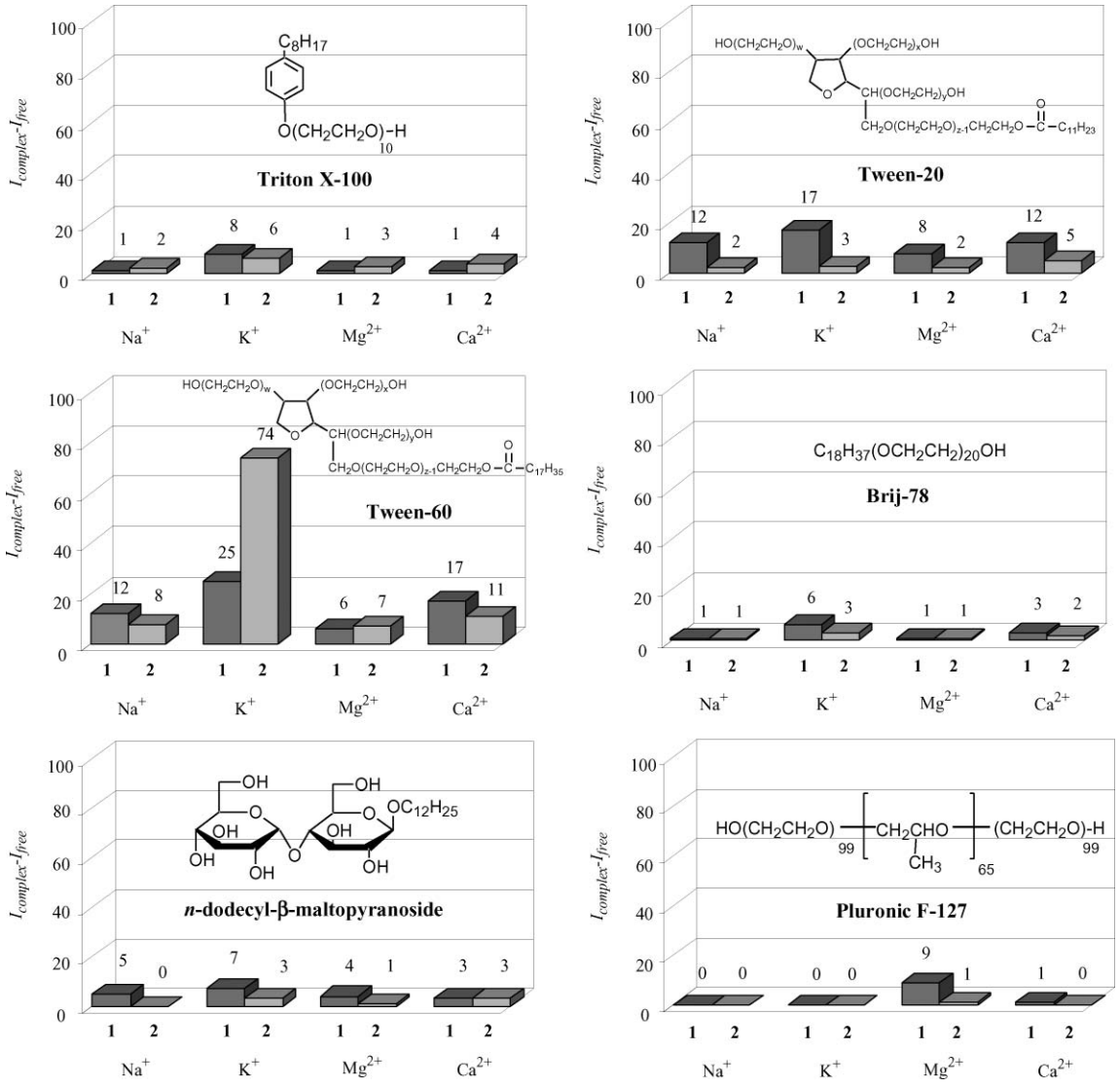


Fig. 5 CHEF effects of **1** (1.0×10^{-6} M) and **2** (1.0×10^{-6} M) with chloride salts (1.0×10^{-3} M, 1000 equiv.) of alkali metal and alkaline earth metal cations in Tris solutions (1.0×10^{-2} M Tris, pH = 10.2) in the presence of Triton X-100 (1.0×10^{-3} M), Tween-20 (1.0×10^{-3} M), Tween-60 (1.0×10^{-3} M), Brij-78 (1.0×10^{-3} M), *n*-dodecyl-β-maltopyranoside (1.0×10^{-3} M), and Pluronic F-127 (1 mg mL^{-1}). Excitation wavelength: 342 nm.

the monoazacryptand-type fluorophores showed relatively large CHEF effects as compared to those in the presence of other non-ionic surfactants. In particular, **2** showed excellent K^+ selectivity in aqueous micellar solutions of Tween-60. To investigate the effects of the pore size of the monoazacryptands, the selectivity towards all alkali metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+) was examined. Fig. 6 showed that the largest CHEF effects of **1** and **2** were observed upon the addition of Rb^+ and K^+, respectively, which suggests that the amino nitrogen atom is effectively coordinated to the metal cation in these cases. Therefore, it is expected that the pore sizes of **1** and **2** are similar to the ionic sizes of Rb^+ and K^+, respectively. Previously, we examined the metal cation selectivity of this type of monoazacryptand using solvent extraction experiments,[10a] but no clear metal

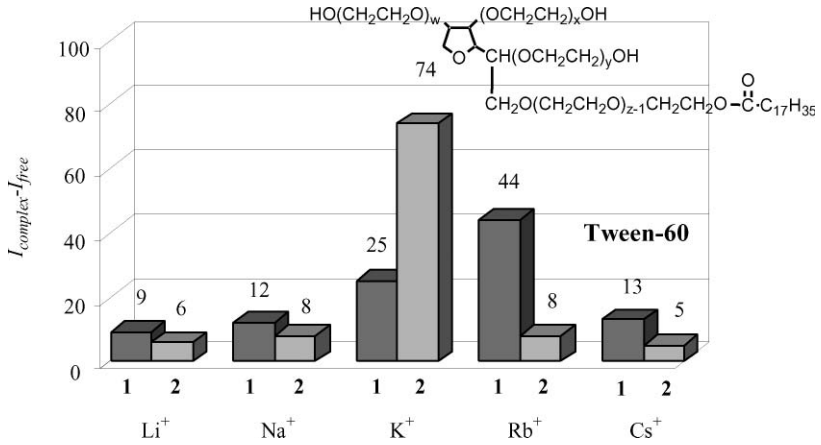


Fig. 6 CHEF effects of **1** (1.0×10^{-6} M) and **2** (1.0×10^{-6} M) with chloride salts (1.0×10^{-3} M, 1000 equiv.) of alkali metal cations in Tris solutions (1.0×10^{-2} M Tris, pH = 10.2) in the presence of Tween-60 (1.0×10^{-3} M). Excitation wavelength: 342 nm.

cation selectivity was observed at that time. In this study, the metal cation selectivity of monoazacryptand-type fluorophores was determined from the fluorescence intensity changes upon the addition of metal cations in aqueous micellar solutions of Tween-60.

In the presence of Tween-20, *n*-dodecyl-β-maltopyranoside and Pluronic F-127, the CHEF effects of the fluorophores were very small. This result suggests that these surfactants with shorter alkyl chains do not offer sufficient hydrophobic complexation fields for cations to fluorophores. Interestingly, even in the presence of Brij-78, which has the same carbon number of lipophilic groups and the same number of oxyethylene units as Tween-60, the fluorophores showed minimal CHEF effects. To clarify the difference between Tween-60 and Brij-78, the association abilities of the surfactants toward K^+ were examined by UV spectroscopy. The absorption wavelength in the UV spectrum of the picrate anion is a measure of the type of ion pair formed.[19] The surfactant was mixed with potassium picrate in THF, and the maximal wavelength of the picrate anion was plotted (Fig. 7). A larger bathochromic shift of the picrate anion was observed in the presence of Brij-78, which indicates that a loose ion pair of potassium picrate was formed, as compared to that in the presence of Tween-60. In other words, the complexation ability of Brij-78 towards K^+ was stronger than that of Tween-60 in THF. Compounds with a long and linear polyoxyethylene unit are known to form cationic complexes with alkali metal and alkaline earth metal cations similar to crown ethers.[20] Thus, it can be hypothesized that Tween-60, which has a branched polyoxyethylene unit, gives the host compounds more effective complexation fields for cations than Brij-78, which has a linear polyoxyethylene unit that can interrupt the complexation between fluorophores and metal cations. When the corresponding monoazacrown ethers **3** and **4** were used instead

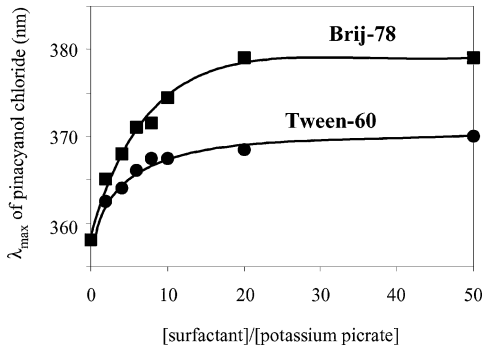


Fig. 7 Plots of the wavelength of maximal absorption (λ_{max}) of potassium picrate (5.0×10^{-5} M) with different concentrations of surfactants in THF.

of **1** and **2**, the addition of all metal cations barely showed any CHEF effects in aqueous micellar solutions of Triton X-100 and Tween-60. This result demonstrates that the cryptand scaffold is necessary for the detection of metal cations, even in aqueous micellar solutions of Tween-60, which creates effective complexation fields for cations.

In the presence of anionic surfactants, it is probable that anionic charges are present at the micellar interface, and this micelle region becomes favorable as a complexation field for cations. This may be the reason why target metal cations are concentrated at the micelle interface by the electrostatic attractive force of the anionic charges on the surfactants. However, it is also possible that the counter cations of the anionic surfactants may interfere with the host–guest (target metal cations) interaction. In fact, in the presence of SDS, a strong fluorescence of **1** was observed, even in the absence of additional metal cations, whereas the fluorescence of **2** remained fully quenched. This result demonstrates that **1** (derived from 18-crown-6 ring) can complex with the counter cations (Na^+) of SDS to cause a recovery of the fluorescence, but **2** (derived from 15-crown-5 ring) could barely complex with Na^+. Therefore, we chose **2** as a fluorescent indicator for metal cations in aqueous micellar solutions of anionic surfactants.

Fig. 8 shows the CHEF effects upon the addition of metal cations in aqueous micellar solutions of various anionic surfactants. **2** showed relatively high CHEF effect with Ca^{2+} in the presence of SDBS and NaDC, but showed little CHEF effects with all other metal cations in the presence of SDS and NaC. This result suggests that the larger hydrophobic portions of SDBS and NaDC, when compared with SDS and NaC, may give the fluorophores more effective complexation fields for cations. To lower the effects of the counter cations, TMADS and TMADC, which have tetramethylammonuim ions as the counter cations, were used. Since cryptands have little complexation ability with quaternary ammonium, it is expected that an inhibition of the formation of the fluorophore–metal complex by the counter cations will be weakened. In the presence of both surfactants, **2** showed very large CHEF effects with Mg^{2+}. Overall, there was a tendency that **2** detected alkaline earth metal cations more effectively than alkali metal cations in aqueous micellar solutions of anionic surfactants. This result may be due to an enhancement of the electrostatic interaction between the anionic surfactants and alkaline earth metal cations, which have a larger charge density.

In the presence of cationic micelles, it is probable that cationic charges are present at the micellar interface, and the micelle becomes unfavorable as a complexation field for cations. This may be the reason why it is difficult for target metal cations to approach the micellar interface because of the electrostatic repulsion between metal cations and the cationic charges on the

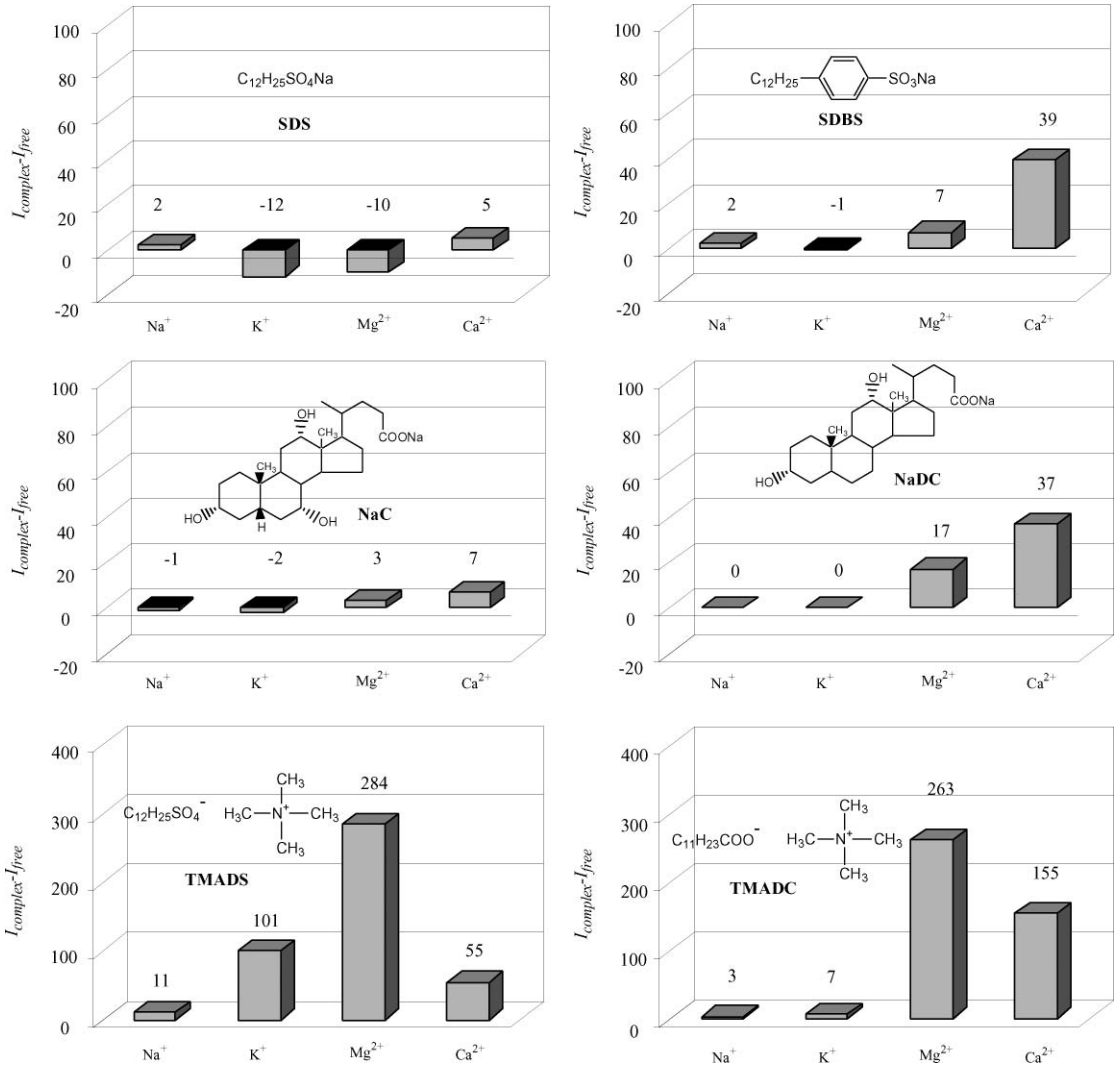


Fig. 8 CHEF effects of **2** (1.0×10^{-6} M) with chloride salts (1.0×10^{-3} M, 1000 equiv.) of alkali metal and alkaline earth metal cations in Tris solutions (1.0×10^{-2} M Tris, pH = 10.2) in the presence of SDS (8.3×10^{-3} M), SDBS (1.3×10^{-3} M), NaC (1.1×10^{-2} M), NaDC (4.0×10^{-3} M), TMADS (5.4×10^{-3} M), and TMADC (2.5×10^{-2} M). Excitation wavelength: 342 nm.

surfactants. In fact, both fluorophores failed to detect all kinds of metal cations in aqueous micellar solutions of CTAB.

Conclusions

In conclusion, we have developed a novel fluorescent detection device for metal cations in aqueous media by combining pyrene-functionalised monoazacryptands and micelles formed by nonionic and anionic surfactants. Three-dimensionally preorganaized monoazacryptand **1** (derived from 18-crown-6) exhibited very high selectivity and sensitivity towards Ba^{2+} among all alkali metal and alkaline earth metal cations in aqueous micellar solutions of Triton X-100. In consideration of the effects of the Triton X-100 concentration, it was found that the fluorescence intensity of the **1**–Ba^{2+} complex began to recover above the cmc. So, it became clear that the presence of the micelle was indispensable for this fluorescent detection system.

With respect to the selective fluorescent detection of important metal cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) relevant to living organisms, **2** (derived from 15-crown-5) was found to detect K^+ with high selectivity in aqueous micellar solutions of Tween-60. Tween-60 is comprised of a long alkyl chain and branched polyoxyethylene unit, and Tween-60 micelles gave the host compounds the effective complexation fields for cations in water. In the presence of anionic surfactants, **2** showed specific Ca^{2+} and Mg^{2+} selectivity in aqueous micellar solutions of SDBS and TMADS, respectively. As a result, selectivity for a variety of metal cations was achieved. It is hopeful that this new fluorescent detection system will be utilized not only for simple ion sensing, but also for the microscopic evaluation of naturally occurring chemical processes in biological systems.

Experimental

General

^{1}H NMR spectra were recorded with a JEOL GSX-400 (400 MHz) spectrometer using $CDCl_3$ and tetramethylsilane (TMS) as a solvent and an internal standard, respectively. IR spectra were measured on a Horiba FT-710 spectrometer. Mass spectra were measured on a JEOL JMS DX-303 mass spectrometer. Elemental analyses were performed on a Yanagimoto CHN-Corder. The fluorescence measurements were carried out on a Shimadzu fluorescence spectrophotometer (RF-1500). Fluorescence intensities at 394 nm of 1.0×10^{-6} M fluorophore in micelles solutions (excitation wavelength, 342 nm) were recorded both in the absence and presence of metal cations. The UV-visible spectra of different concentrations of surfactant solutions, including 5.0×10^{-5} M potassium picrate, were measured with a Hitachi U-3010 spectrophotometer. All chemicals were of commercially available reagent grade and the surfactants, polyoxyethylene(10) isooctylphenyl ether (Triton X-100), polyoxyethylene(20) sorbitan monolaurate (Tween-20), polyoxyethylene(20) sorbitan

monostearate (Tween-60), polyoxyethylene(20) stearyl ether (Brij-78), *n*-dodecyl-β-maltopyranoside, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer (Pluronic F-127), and sodium dodecyl sulfate (SDS), sodium *n*-dodecylbenzenesulfonate (SDBS), sodium cholate (NaC), sodium deoxycholate (NaDC), and cetyltrimethylammonium bromide (CTAB) were used without further purification. Tetramethylammonium dodecyl sulfate (TMADS)[21] and tetramethylammonium dodecanoate (TMADC)[22] were prepared as previously described.

General procedure for the preparation of monoazacryptands (6)

A solution of diethanolamine (14.7–21.1 mmol) and *cis*-bis(bromomethyl)-dimethyl-crown ethers **5** (4.91–7.05 mmol) in diglyme (80 mL) was added dropwise to a suspension of diglyme (80 mL) containing NaH (29.4–42.3 mmol) over a 5 h period at 120 °C. The mixture was stirred at that temperature for another 24 h. The insoluble matter was removed by filtration, and diglyme was evaporated *in vacuo*. The residue was purified by chromatography over alumina (chloroform).

1,11-Dimethyl-3,6,9,13,19,21,24,27-octaoxa-16-azabicyclo-[9.9.7]heptacosane (6a). By following the general procedure, **6a** was obtained from **5a** as a slightly yellowish viscous liquid in 28% yield; ^{1}H NMR: ($CDCl_3 + D_2O$) δ 1.08 (s, 6H), 2.79 (t, 4H, $J = 5.1$ Hz), 3.32–3.85 (m, 28H); IR: (neat, cm^{-1}) 3560–3300, 2880, 1960, 1660, 1450, 1360, 1300, 1090, 750; MS (FAB) (*m*/*z*, relative intensity) 422 ($M^+ + 1$, 100); Anal. Calcd for $C_{20}H_{39}NO_8 \cdot H_2O$: C, 54.65; H, 9.40; N, 3.19. Found: C, 54.53; H, 9.33; N, 3.19%.

1,11-Dimethyl-3,9,12,15,18,20,23-heptaoxa-6-azabicyclo[9.7.6]-tetracosane (6b). By following the general procedure, **6b** was obtained from **5b** as a slightly yellowish viscous liquid in 68% yield; ^{1}H NMR: ($CDCl_3 + D_2O$) δ 1.09 (s, 6H), 2.72–2.89 (m, 4H), 3.29–3.91 (m, 24H); IR: (neat, cm^{-1}) 3530–3240, 2880, 1660, 1450, 1360, 1290, 1100, 760; MS (FAB) (*m*/*z*, relative intensity) 378 ($M^+ + 1$, 100); Anal. Calcd for $C_{18}H_{35}NO_7$: C, 57.27; H, 9.35; N, 3.71. Found: C, 57.10; H, 9.38; N, 3.44%.

General procedure for the synthesis of 1–4

A THF–toluene solution (30 mL, 1 : 1 v/v) of **6** (1.59–1.97 mmol) or **7** (1.82–3.04 mmol), and triethylamine (1–2 mL), 1-bromomethylpyrene (4.77–9.11 mmol) was refluxed for 12 h. After cooling to room temperature, the mixture was filtered and the solvent was evaporated. The crude product was purified by chromatography over alumina (benzene : ethyl acetate = 98 : 2–90 : 10).

16-(1-Pyrenylmethyl)-1,11-dimethyl-3,6,9,13,19,21,24,27-octaoxa-16-azabicyclo[9.9.7]heptacosane (1). By following the general procedure, **1** was obtained from **6a** as a slightly yellowish viscous liquid in 57% yield; ^{1}H NMR: ($CDCl_3$) 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}) 3040, 2820, 1930, 1740, 1590, 1450, 1370, 1300, 1040, 850, 710; MS (FAB) (*m*/*z*, relative intensity) 636 ($M^+ + 1$, 66), 215 (100); Anal. Calcd for $C_{37}H_{49}NO_8$: C, 69.90; H, 7.77; N, 2.20. Found: C, 69.96; H, 7.79; N, 1.91%.

6-(1-Pyrenylmethyl)-1,11-dimethyl-3,9,12,15,18,20,23-heptaoxa-6-azabicyclo[9.7.6]tetracosane (2). By following the general procedure, **2** was obtained from **6b** as a slightly yellowish viscous liquid in 40% yield; ^{1}H NMR: ($CDCl_3$) δ 1.06 (s, 6H), 2.90–2.96 (m, 4H), 3.33–3.93 (m, 24H), 4.29 (s, 2H), 7.95–8.56 (m, 9H); IR: (neat, cm^{-1}) 3040, 2860, 1930, 1740, 1590, 1450, 1370, 1290, 1100, 850, 710; MS (FAB) (*m*/*z*, relative intensity) 592 ($M^+ + 1$, 48), 215 (100); Anal. Calcd for $C_{35}H_{45}NO_7$: C, 71.04; H, 7.67; N, 2.37. Found: C, 70.81; H, 7.69; N, 2.22%.

***N*-(1-Pyrenylmethyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (3).** By following the general procedure, **3** was obtained from **7a** as a slightly yellowish viscous liquid in 42% yield; ^{1}H NMR: ($CDCl_3$) δ 2.91 (t, 4H, $J = 5.9$ Hz), 3.57–3.71 (m, 20H), 4.35 (s, 2H), 7.94–8.60 (m, 9H); IR (neat, cm^{-1}) 3040, 2860, 1930, 1740, 1590, 1450, 1370, 1290, 1100, 850, 710; MS (FAB) (*m*/*z*, relative intensity) 478 ($M^+ + 1$, 48), 215 (100); Anal. Calcd for $C_{29}H_{35}NO_5$: C, 72.93; H, 7.39; N, 2.93. Found: C, 72.66; H, 7.20; N, 2.79%.

***N*-(1-Pyrenylmethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (4).** By following the general procedure, **4** was obtained from **7b** as a slightly yellowish viscous liquid in 67% yield; ^{1}H NMR: ($CDCl_3$) δ 2.92 (t, 4H, $J = 5.9$ Hz), 3.37 (s, 4H), 3.53–3.70 (m, 12H), 4.35 (s, 2H), 7.95–8.58 (m, 9H); IR (neat, cm^{-1}) 3040, 2840, 1930, 1740, 1590, 1450, 1350, 1290, 1100, 850, 710; MS (FAB) (*m*/*z*, relative intensity) 434 ($M^+ + 1$, 69) 215 (100); Anal. Calcd for $C_{27}H_{31}NO_4$: C, 74.00; H, 7.21; N, 3.23. Found: C, 73.90; H, 7.00; N, 3.15%.

Measurement of fluorescence spectra

The fluorescence spectra were measured at room temperature. The concentration of fluorescent reagents was 1×10^{-6} M in the surfactant solutions (1×10^{-3} M). Alkali metal cations and alkaline earth metal cations were added into the solution of fluorescent reagent as perchlorate salts (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), thiocyanate salts (Li^+, Na^+, K^+, Rb^+, Cs^+), and chloride salts (Na^+, K^+, Mg^{2+}, Ca^{2+}). To prevent nonlinearity of the fluorescence intensities, the excitation wavelength was set to 342 nm.

Measurement of stability constants

All of the stability constants reported herein were determined from a curve of the fluorescence intensity by means of a nonlinear least-square curve fitting method. Typically, the concentration of the host compound was fixed at 1×10^{-6} M, and the molar ratios of the guest to host were changed by changing the concentrations of the guest salt. Eight data were collected for each host–guest system and the stability constant (K) was calculated using an iterative nonlinear least squares curve-fitting program.[16]

Measurement of UV

All UV spectra were measured at room temperature. The concentration of potassium picrate was fixed at 5×10^{-5} M in THF. The molar ratios of the surfactant to potassium picrate were changed in the range from 0 to 50 by changing the concentrations of the surfactant.

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