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New Hg^{2+}-selective fluoroionophores derived from *p-tert*-butylcalix[4]arene–azacrown ethers

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New fluorogenic ionophores based upon the *p-tert*-butylcalix[4]arene–azacrown ethers having anthrylmethyl moieties as the fluorophore have been prepared and their fluoroionophoric properties were investigated. Diazacrown-based derivative **5** exhibited a relatively well-optimized sensing behaviour towards Hg^{2+} ions compared with the triazacrown analogue **6**. A fluorescence enhancement of about 87-fold was observed for the **5**-Hg^{2+} system in a MeOH–THF mixed solvent system.

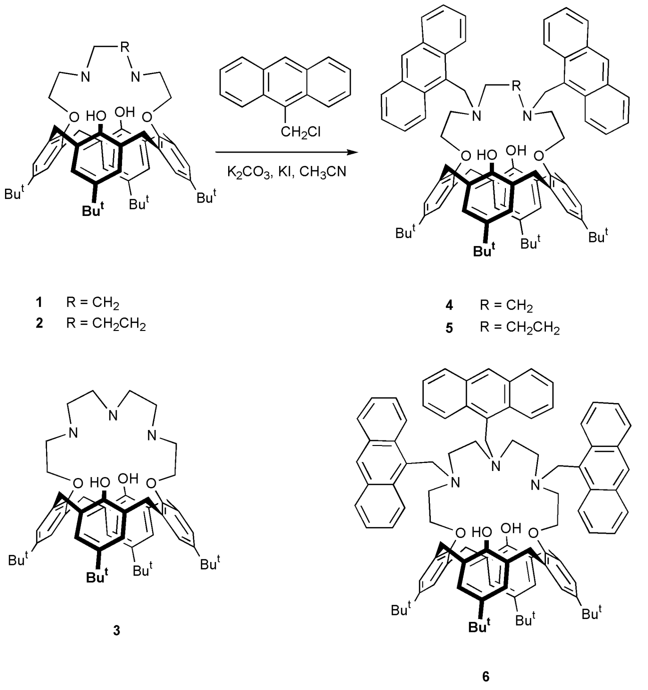
Introduction

The development of optical sensors for the selective determination of heavy metal ions is very important for the detection and treatment of environmental contamination.[1,2] Numerous examples of chromogenic and fluorogenic ionophores have been designed but the latter are more desirable for their intrinsic sensitivity and selectivity in signal transduction functions. Much effort has been focused on developing new and efficient fluoroionophores for targeting ions of specific importance in a variety of fields such as medical analysis and environmental monitoring.[3–6] Among many candidates, anthracene groups are one of the most attractive fluorophores due to their strong fluorescence and relatively well characterized photophysical properties. Earlier examples of cyclic azacrown ether moieties linked to an anthracene unit as a fluorophore by a methylene group showed unique chelation-enhanced fluorescence on complexation with guest metal ions.[7–9] In these classical observations, the compounds are designed to have nearby amine moieties which upon complexation with metal ions are unable to donate an electron to the excited state of the anthracene fluorophore. Calixarenes[10] having anthryl groups have also been reported by several research groups and their ionophoric properties towards a variety of metal ions including Na^+, Cs^+, some transition metal ions and chiral amines have been investigated.[11–14] We have recently prepared and found that *p-tert*-butylcalix[4]arene–azacrown ethers and its chromogenic azophenol derivative have high selectivity towards Hg^{2+} ions over other heavy and transition metal ions as carrier and chromoionophore, respectively.[15,16] We postulated that by appropriately combining the basic skeleton of calix–azacrown ethers with anthryl fluorophores new fluorogenic ionophores for the sensing of heavy metal ions would result. Here we report the synthesis of a series of *p-tert*-butylcalix[4]arene–azacrown ethers having appended anthrylmethyl groups and their selective fluoroionophoric properties towards Hg^{2+} ions.

Results and discussion

Syntheses of ionophores

The reaction of azacrown ethers **1**–**3**[15] with a slight excess of 9-(chloromethyl)anthracene (KI, K_2CO_3–CH_3CN) afforded the desired bis(anthrylmethyl) derivatives **4**, **5** and tris(anthrylmethyl) derivative **6** in good yields (76–82%) (Scheme 1). Products were purified by repeated recrystallization from CH_2Cl_2–CH_3OH. The ^1H NMR resonances of the anthryl derivatives, particularly for the azacrown ether part, were significantly broadened perhaps as a result of the reduced molecular flexibility of the resulting compounds. For compound **6** some of the ^1H resonances for the anthracene ring and methylene protons of anthrylmethyl moieties are well resolved into a pair of resonances in a 1 : 2 ratio as expected from its molecular symmetry. As the recognition site of **4**–**6** for the discrimination of the guest metal ions is mainly based on the molecular framework of the *p-tert*-butylcalix[4]arene–azacrown ether moieties we expected them to have a high binding selectivity towards some transition metal and heavy metal ions such as Hg^{2+}.[15–17] In addition to this, we thought that the employment of a calix[4]arene backbone would provide a useful handle for further functionalization of the resulting molecule by utilizing the versatile reactivity of the phenolic moiety to yield valuable supramolecular systems, such as nitro and quinone derivatives, having dual function of spectroscopic and electrochemical responses towards given target guests.



Scheme 1

Fluoroionophoric properties

The ionophoric properties of anthryl derivatives were investigated by fluorescence measurements in the presence of varying metal ions. The anthryl derivatives **4**–**6** showed a series of absorption bands characteristic of the anthracene group around 350–385 nm in THF, acetonitrile and CH_3OH. First, the fluorescence behaviour of the free host **5**, itself having a propylene linkage in the azacrown moiety, was measured in CH_3OH–THF (9 : 1, v/v, 1.0×10^{-5} mol dm^{-3}, $\lambda_{ex} = 340$ nm) and found to have very weak fluorescence. This is in good agreement with the well-established fact that anthracene groups having nearby amine functions show very weak fluorescence due to effective quenching by the amino group.[7] Upon interaction of **5** with 100 equiv. of representative alkali (Li^+, Na^+, K^+, Rb^+, Cs^+), alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), transition (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and heavy metal (Cd^{2+}, Pb^{2+}, Hg^{2+}) ions in perchlorate, the fluorescence was considerably affected and the representative results are given in Fig. 1. Among the tested metal ions, Hg^{2+} revealed a particularly large fluorescence enhancement. The resulting increases in fluorescence intensity of **4**–**6** induced by the metal ions at 422 nm are depicted in Fig. 2 as the ratio of the fluorescence intensities in the presence (I) and the absence (I_o) of metal ions.[18]

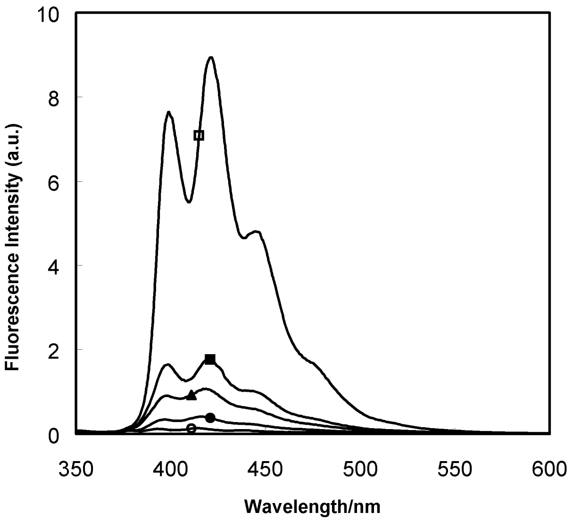


Fig. 1 Fluorescence spectra of **5** in the absence (○) and presence of Hg^{2+} (□), Cu^{2+} (■), Pb^{2+} (▲) and Zn^{2+} (●) ions. [**5**] = 1.0×10^{-5} mol dm^{-3}; [M^{2+}] = 1.0×10^{-3} mol dm^{-3}; in CH_3OH–THF (9 : 1, v/v).

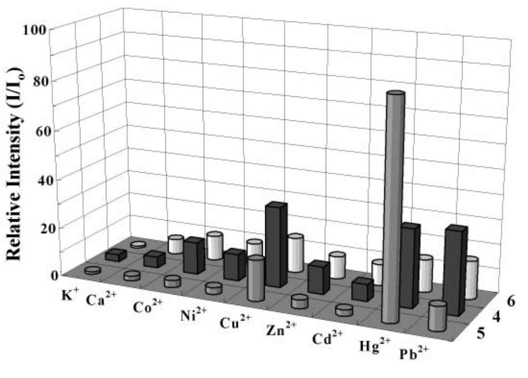


Fig. 2 Fluorescence enhancement ratios (I/I_o) for the ionophores **4**–**6** for the representative guest metal ions at 422 nm; $\lambda_{ex} = 340$ nm in CH_3OH–THF (9 : 1, v/v).

As can be seen from Fig. 2, Hg^{2+} ions induced a marked fluorescence enhancement that is attributable to the fact that complexation of metal ions by the nitrogen atoms of the azacrown moiety results in the effective inhibition of the quenching process. The ratio (I/I_o) for Hg^{2+} is around 87-fold which is comparable to many related systems and is sufficiently large for the efficient detection of this metal ion in many chemical systems. The next largest increases in fluorescence intensity of **5** were induced with Cu^{2+} followed by Pb^{2+} ions ($I/I_o = 16.8$ and 9.9, respectively). For the rest of transition metal ions, the I/I_o values are less than 3.6 and are not so pronounced. Other metal ions investigated showed relatively negligible influence on the fluorescence spectral properties of the ionophore (*i.e.*, for alkaline earth metal ions, $I/I_o < 2.0$ and for alkali metal ions, $I/I_o < 1.7$, data not shown). These observations suggest that **5** could be used as a selective fluorogenic sensor for the detection of Hg^{2+} ions in a variety of chemical systems.

During the process of searching for the optimized solvent system for **5**, other solvent systems tested were found to produce a much reduced selectivity toward Hg^{2+} compared to the CH_3OH–THF system (Fig. 3). With 100 equiv. of Hg^{2+} ions in THF, the I/I_o ratio increases up to 141-fold; this significantly increased enhancement in fluorescence intensity, compared to the CH_3OH–THF system, is possibly due to a somewhat enhanced stability of the **5**-Hg^{2+} complex in this less polar solvent system. However, with the THF system, other metal ions including Cu^{2+} ($I/I_o = 136$), Co^{2+} ($I/I_o = 86$) and Zn^{2+} ($I/I_o = 48$) in addition to Hg^{2+} ions, also showed greatly increased fluorescence enhancements and hence there is a drastic decrease in selectivity of **5** towards Hg^{2+} ions. Meanwhile, with CH_3CN–THF (9 : 1, v/v) as the solvent system, **5** again exhibited a large enhancement towards the target Hg^{2+} ions ($I/I_o = 126$) but with significant responses to the other metal ions, particularly towards Cu^{2+} ($I/I_o = 95$) and Pb^{2+} ($I/I_o = 55$).

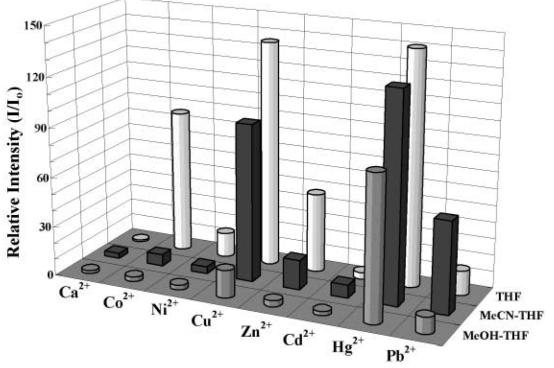


Fig. 3 Fluorescence enhancement ratios (I/I_o) of the ionophore **5** in varying solvent systems for the representative guest metal ions at 422 nm; $\lambda_{ex} = 340$ nm. MeCN–THF and MeOH–THF denote CH_3CN–THF (9 : 1, v/v) and MeOH–THF (9 : 1, v/v), respectively.

It is well known that the geometry of the spacers between the donor atoms in crown ethers significantly affects the ion binding properties of the resulting ionophore systems.[19] To gain an insight into the effect of structural variation on their recognition behaviour, the closely related diazacrown **4** and triazacrown ether derivatives **6** were prepared and their fluorogenic properties were also investigated (Fig. 2). The compounds **4** and **6** themselves also showed very weak fluorescence intensity due to similar quenching by the neighbouring amine functions in CH_3OH–THF (9 : 1). Upon interaction of **4** and **6** with the guest metal ions investigated, the fluorescence intensities increase significantly, as is the case for **5**. However, the fluorescence enhancements of **4** and **6** for Hg^{2+} are not so large compared with **5** and the maximum enhancements for **4** and **6** in CH_3OH–THF (9 : 1) are about 37 and 16%, respectively, of the value obtained for **5**. Furthermore, quite distinct from the Hg^{2+}- and Cu^{2+}-selective fluorogenic behaviour of **5**, compounds **4** and **6** showed more plateau-type non-discriminating responses towards the examined metal ions. For **6**, the relatively high affinity of the triazacrown ether moiety, having three nitrogen amine donor atoms, for many of the metal ions seems to induce significant fluorescence responses towards a range of competing transition and heavy metal ions. This results in poor selectivity for the target metal ions in spite of the increased number of ligating nitrogen donor atoms in the triazacrown **6**.

The binding strengths of the most discriminating ionophore **5** towards metal ions were determined by following the changes in fluorescence spectra. As can be seen from Fig. 4 for the **5**-Hg^{2+} system in CH_3OH–THF (9 : 1), the fluorescence intensity increases progressively with the increase in Hg^{2+} concentration. From this titration, the association constant for the **5**-Hg^{2+} complex system was determined by the nonlinear curve fitting procedure[20] and found to be 1.8 × 10^3 mol^{-1} dm^3. Although the association constant of the **5**-Hg^{2+} system is not so suitable for trace analysis of Hg^{2+} ions at the submillimolar level, it seems to be suitable for the analysis of millimolar concentrations of analytes frequently found in many chemical systems. In fact, the detection limit of **5** for Hg^{2+} ions was found to be 6 × 10^{-5} mol dm^{-3} as determined from the plot of fluororescence changes as a function of metal ion concentration.[21] For the other metal ions having somewhat weaker responses, K_a values for **5** in the CH_3OH–THF (9 : 1) solvent system were found to be 2.8 × 10^3 (Cd^{2+}), 8.6 × 10^3 (Pb^{2+}), 6.1 × 10^3 (Zn^{2+}), 8.3 × 10^3 (Cu^{2+}), 7.4 × 10^3 (Ni^{2+}), 5.0 × 10^3 (Co^{2+}) and 2.4 × 10^3 (Ca^{2+}) mol^{-1} dm^3, respectively. The ionophore **5** showed relatively similar K_a values for the examined transition and heavy metal ions that might be due to the relatively simple ionophoric structure consisting of two nitrogen donor atoms of the azacrown moiety and possibly two oxygen donor atoms of phenol functions. In other solvent systems, the K_a value for the **5**-Hg^{2+} system decreases as the polarity of the medium increases and the observed association constants were 5.8 × 10^4 mol^{-1} dm^3 (CH_3CN–THF 9 : 1, v/v) and 2.4 × 10^4 mol^{-1} dm^3 (THF). In the CH_3OH–THF (9 : 1, v/v) system, the relatively high polar nature of the medium significantly reduced the strength of the complexes formed, but the results obtained suggest that the selectivity in fluorescence response toward Hg^{2+} is enhanced. The binding affinity of **5** towards the target metal ions was further supported by FAB mass spectrometric measurements. The FAB mass spectrum of **5** observed under competitive conditions [in 3-nitrobenzyl alcohol (*m*NBA)] in the presence of a mixture of metal ions of Cu^{2+} and Hg^{2+} showed a prominent peak at *m*/*z* = 1217.1 for the [**5**-H + Cu]$^+$ complex compared with very weak peaks for the **5**-Hg^{2+} and related species. This observation also suggests that the **5**-Cu^{2+} complex is more stable than the **5**-Hg^{2+} complex under present experimental conditions. Because the fluorescence enhancements are not parallel to the association constants, unfortunately, we could not make a clear-cut reasoning for the exact nature and mechanism of the fluorescence behaviour at the moment. The fluorescence behaviour in the present system seems to be affected in a complicated manner both by the general quenching effects of the transition metal ions and the possible enhancements exerted by the coordination of the azacrown moiety on the nitrogen lone pair electrons.[9,22]

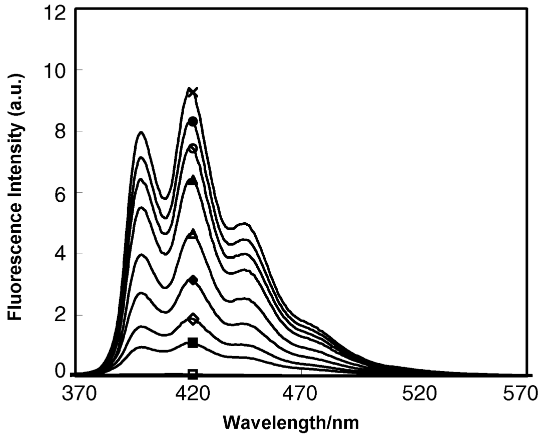


Fig. 4 Fluorescence spectra of **5** in CH_3OH–THF (9 : 1, v/v) upon interaction with incremental Hg^{2+} ions. [**5**] = 1.0 × 10^{-5} mol dm^{-3}. [Hg^{2+}]/**5**: 0, (□); 10, (■); 25, (◇); 50 (◆); 100, (△); 200, (▲); 300, (○); 500, (●); 1000, (×).

One more thing to note is that treatment of the solution with EDTA readily scavenges the complexed metal ions of Hg^{2+} and Cu^{2+} which results in full restoration of the fluorescence spectrum of **5** itself. This observation suggests the easy regeneration and reusability of the fluoroionophore **5** in the sensing of the Hg^{2+} ions. We also tried to obtain information about the selective complexation of **5** toward Hg^{2+} ions by ^1H NMR spectroscopy but failed to obtain meaningful data due to the significant broadening and small changes in the chemical shifts during the titration process.

In summary, the anthryl-appended *p*-*tert*-butylcalix[4]arene–diazacrown ether derivative **5** exhibited pronounced selective and sensitive fluoroionophoric properties toward Hg^{2+} ions. Furthermore, in the present system the signalling mode is the OFF–ON type, which is known to be more beneficial than ON–OFF type transductions. The former mode is relatively free from possible uncertainties originating from other interfering species.[23] The designed dianthryl compound **5** seems to be relatively well-optimized for the recognition of Hg^{2+} ions over other common interfering metal ions and can be used as a novel optical sensory material for the detection of toxic mercury ions in a variety of chemical systems.

Experimental

General

^1H NMR (300 MHz) spectra were measured on a Varian Gemini-2000 spectrometer. Microanalyses were accomplished at the Basic Science Center, Chung-Ang University. The FAB mass spectra were obtained (from an *m*NBA matrix) with a Micromass Autospec Mass Spectrometer. Melting points were measured using a Fischer-Johns Melting Point Apparatus. THF was purchased from Aldrich Chemical Co. as 'anhydrous' and stored over 4 Å molecular sieves and dichloromethane was freshly distilled from CaH_2. Other simple chemicals were purchased and used as received. All experiments were carried out under an atmosphere of nitrogen. For TLC analysis, Merck pre-coated TLC plates (silica gel 60 GF 254, 0.25 mm) were used. Azacrown ether derivaitves of calix[4]arene **1**–**3**[15] were prepared by the reduction of corresponding cyclic amide derivatives.[24]

Preparation of anthrylmethyl derivatives (4–6)

Compound **4** was prepared by refluxing a mixture of diazacrown ether **1** (300 mg, 0.39 mmol), 9-(chloromethyl)anthracene (197 mg, 0.87 mmol), KI (65 mg, 0.39 mmol) and K_2CO_3 (109 mg, 0.79 mmol) in CH_3CN (30 mL) for 4 h under a nitrogen atmosphere. After cooling, the reaction mixture was partitioned between CH_2Cl_2 and water. The organic phase was washed with water and the solvent was evaporated. The residue was purified by repetitive recrystallization from CH_2Cl_2–CH_3OH to yield light yellow crystals (360 mg, 80% yield); mp 291 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.03 and 1.26 (s, 18H each, $C(CH_3)_3$), 3.07 (d, 4H, $J = 12.6$ Hz, $ArCH_2Ar$), 3.26 (br m, 4H, NCH_2CH_2O), 3.45 (br m, 4H, NCH_2CH_2O), 3.72 (s, 4H, NCH_2CH_2N), 3.92 (d, 4H, $J = 12.3$ Hz, $ArCH_2Ar$), 4.75 (s, 4H, anthryl-CH_2), 6.84 and 6.96 (s, 4H each, ArH), 8.38 (s, 2H, OH), 7.28–8.63 (m, 18H, anthryl-H); FAB-MS (*m*NBA), *m*/*z* found 1141.5 (100%) [M + H]$^+$. Anal. Calcd for $C_{80}H_{88}N_2O_4$: C, 82.86; H, 7.82; N, 2.42. Found: C, 83.28; H, 7.80; N, 2.53%.

Compounds **5** and **6** were prepared similarly by the reaction of **2** and **3**, respectively, with 9-chloromethylanthracene. Diazacrown ether **5**: yield 82%; mp 288 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 and 1.31 (s, 18H each, $C(CH_3)_3$), 2.59 (br m, 2H, $NCH_2CH_2CH_2N$), 2.90 (d, 4H, $J = 12.6$ Hz, $ArCH_2Ar$), 3.05 (br m, 4H, $NCH_2CH_2CH_2N$), 3.20 (br m, 4H, NCH_2CH_2O), 3.35 (br m, 4H, NCH_2CH_2O), 3.83 (d, 4H, $J = 12.9$ Hz, $ArCH_2Ar$), 4.71 (s, 4H, anthryl-CH_2), 6.59 and 6.96 (s, 4H each, ArH), 7.30–8.69 (m, 20H, anthryl-H and OH); FAB-MS (*m*NBA), *m*/*z* 1155.6 (100%) $[M + H]^+$. Anal. Calcd for $C_{81}H_{90}N_2O_4\cdot 0.5\ H_2O$: C, 83.55; H, 7.88, N, 2.41. Found: C, 83.01; H, 7.90; N, 2.45%. Triazacrown ether **6**: yield 76%; mp 164 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79 and 1.35 (s, 18H each, $C(CH_3)_3$), 2.98 (d, 4H, $J = 12.6$ Hz, $ArCH_2Ar$), 3.00 and 3.14 (br m, 4H each, NCH_2CH_2N), 3.39 (br m, 4H each, NCH_2CH_2O and NCH_2CH_2O), 4.13 (d, 4H, $J = 13.5$ Hz, $ArCH_2Ar$), 4.28 and 4.53 (s, 4H and 2H, anthryl-CH_2), 6.55 and 7.03 (s, 4H each, ArH), 6.88 (s, 2H, OH), 7.30–8.56 (m, 27H, anthryl-H); FAB-MS (*m*NBA), *m*/*z* 1374.7 (83%) $[M + H]^+$. Anal. Calcd for $C_{97}H_{103}N_3O_4\cdot 0.5\ H_2O$: C, 84.19; H, 7.58; N, 3.04. Found: C, 84.18; H, 7.58; N, 3.12%.

Fluorescence titration experiments

Fluorescence measurements were performed using a Aminco-Bowman Series 2 Spectrometer after degassing the sample with N_2 bubbling. All the solvents used were spectroscopic grade (Aldrich). Incremental amounts of the metal perchlorate solutions (2.0×10^{-2} mol dm^{-3} in CH_3OH) were added to the ionophore solution (1.0×10^{-4} mol dm^{-3} in THF) by micro syringe. After this, calculated amounts of pure solvents were added to make the required concentrations of the ionophore and metal ions, as well as the solvent compositions. The association constants K_a were determined by a nonlinear curve fitting procedure for the changes in fluorescence intensity upon addition of increments of metal ions.[20]

Acknowledgements

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