Preparation of Blue Anthracene Fluoroionophore Containing Calix[4]azacrown and Their Luminescent Properties

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Introduction

Cation sensing has become very important for chemical, biological and environmental applications within the last 35 years.[1] Although a large number of sensors has been developed, a common set of design themes can be identified. In each case one or more signaling centers (fluorophore) have been linked to acyclic, macrocyclic, calixarene or related ligand frameworks (ionophore) capable of analyte binding and fluorescent sensors is thus called a fluoroionophore.[2-6] In the design of such sensors, attention should be paid to both recognition and signaling moieties. The signaling moiety converts the information into an signal expressed as the changes in the photophysical characteristics of the fluorophore.[7] These changes are due to the perturbation by the bound cation of photochemical processes such as electron transfer, charge transfer, energy transfer, excimer or exciplex formation or disappearance, etc.[8] Fluorescent photo-induced electron transfer has been extensively studied. Although quite a large number of reports exists on the crown ether- and cryptand-based PET, those on calix[4]azacrowns are limited.[1,9-11] Moreover, calix[4]azacrown based polymers have just begun to receive attention, as these new polymers may then be processed into materials suitable for the chemical sensor devices such as ion selective electrodes.[12-14] Recently, in our previous work we have synthesized polymeric fluoroionophores having bisazacrown and have investigated their ionophoric properties for alkali and alkali earth metal cations.[15]

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In this paper, novel calix[4]-bis-azacrown-5 containing blue-light emitting anthracene fluorophore, N,N-bis[9-[10-(p-tolyl)anthracenylbenzyl]-calix[4]-bisazacrown-5 (4) and alternating copolymer (5) with similar repeating unit were prepared reacting by calix[4]-bis-azacrown-5 (1) with 2 or 3. Fluorescence emission spectral studies were investigated by binding group I, group II and various metal cations.

Experimental

Materials and Measurements. 9-(p-Bromomethylphenyl)-10-(p-methylphenyl)anthracene (2) and 9,10-bis(p-bromo-methylphenyl)anthracene (3) were prepared by the controlled bromination of 9,10-bis(p-methylphenyl)anthracene with NBS. 1 was prepared by the method previously reported.[16] Tetrahydrofuran and diisopropyl ethylamine (Aldrich Chem. Co.) were distilled over sodium and calcium hydride. FTIR spectra were obtained with a Biorad Excaliber FTS-3000MX spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Unity Inova (200 MHz) spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. UV/Vis spectra were obtained on a Shimadzu 1601PC. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ-Stryragel 10^2, 10^3 and 10^4 Å) in THF and calibrated with polystyrene standards at 20 °C.

Preparation of N,N-bis[9-[10-(p-tolyl)anthracenyl Benzyl]-calix[4]-bisazacrown-5 (4). To a solution of 1 (1.0 g, 1.20 mmol) and diisopropyl ethyl amine (1.30 g, 10 mmol) in THF (100 mL) was added dropwise 2 (1.30 g, 3.0 mmol) in THF (10 mL) over 30 min at 0 °C under nitrogen. Upon complete addition, the reaction solution was stirred for 12 h at 0 °C, and then stirred for an additional 8 h at 65 °C. Removal of THF *in vacuo* gave a yellow powder. The crude product was extracted several times with methylene chloride and water. Column chromatography using methylene chloride/n-hexane (2/3) as an eluent gel gave the desired product as a yellow solid.

Yield 82%. FTIR (KBr, cm⁻¹) 3063 (aromatic C-H), 2930, 2867 (aliphatic C-H), 1131, 1096 (C-O). ^{1}H NMR (CDCl₃, ppm) 7.84-7.26 (m, 32 H, 2 ArH-diphenylanthracene), 7.18-6.95 (m, 12 H, 4 ArH-calix), 3.96 (s, 4 H, Ar-CH_2N-), 3.92-3.85 (m, 24 H, 4 -OCH_2CH_2OCH_2-), 3.80 (s, 16 H, 4 Ar-CH_2-Ar), 2.97 (s, 8 H, 4 -CH_2N-), 2.32 (s, 6 H, 2 -CH_3). Anal. Calcd for C₉₉H₉₅N₂O₈(Mw, 1440.82): C, 82.53%; H, 6.64%; N, 1.94%. Found: C, 82.80%; H, 6.69%; N, 1.91%.

Preparation of Polymeric Fluoroionophore (5). In a three-necked flask was place a solution of 1 (1.00 g, 1.20 mmol) and diisopropyl ethyl amine (1.30 g, 10 mmol) dissolved in DMF. 3 (0.62 g, 1.20 mmol) in DMF (10 mL) was added dropwise slowly through a dropping funnel at 25 °C under

nitrogen. The reaction mixture was heated for 24 h at 120 °C. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered. The resulting polymer was precipitated in ethyl ether and dried *in vacuo* at 60 °C.

Yield 87%. FTIR (KBr, cm^{-1}) 3070, 3022 (aromatic C-H), 2924, 2869 (aliphatic C-H), 1128, 1091, 1055 (C-O), ^{1}H NMR (CDCl$_3$, ppm) 8.15-7.25 (m, 16 H, ArH-diphenylanthracene), 7.19-6.93 (m, 12 H, 4 ArH-calix), 3.95 (s, 4 H, 2 Ar-H_2N-), 3.79 (s, 8 H, 4 Ar-CH_2-Ar), 3.90-3.84 (m, 24 H, 4 -OCH_2CH_2OCH_2-), 2.98 (s, 8 H, 4 -CH_2N-). Anal. Calcd for C$_{71}$H$_{74}$N$_2$O$_8$ (Mw, 1084.36): C, 78.64%; H, 6.88%; N, 2.58%. Found: C, 78.80%; H, 6.89%; N, 2.61%.

Results and Discussion

The introduction of 9,10-diphenylanthracene to the aza-crown frame-work has been reported to produce a powerful binding site for metal ions.[15] This led us to design diphenyl-anthracene-armed calix[4]azacrown ether in which diphenylanthracene-armed azacrown loop links to the 1,3-alternate calix[4]arene frame-work. Starting material calix[4]-bis-azacrown-5, 1 in the 1,3-alternate conformation could be prepared in multi-steps from calix[4]arene.[16] The synthetic scheme for preparing the diphenylanthracene-armed calix-azacrown ether is shown in Scheme I.

The reaction of 1 with 2 in the presence of diisopropyl ethylamine in THF gave the desired product 4 in moderate yield. Also the polymeric fluorophore 5 was prepared by condensation polymerization of 3 with 1 in the presence of diisopropyl ethylamine as shown in Scheme II. Total yields of polymers were found to be moderately high. To the best of our knowledge, these are the first examples of calix[4]aza-crowns with anthracene fluorophore as a pendent arm. The product was confirmed to be in the fixed 1,3-alternate conformation based on ^{1}H NMR, IR spectral assignment and elemental analysis. The incorporation of calix[4]azacrown ether into the polymer backbone enhances the solubility in common organic solvents to a high degree.

Scheme I

1 DIEA DMF **2**

4

Scheme II

3

Et$_3$N
DMF

5
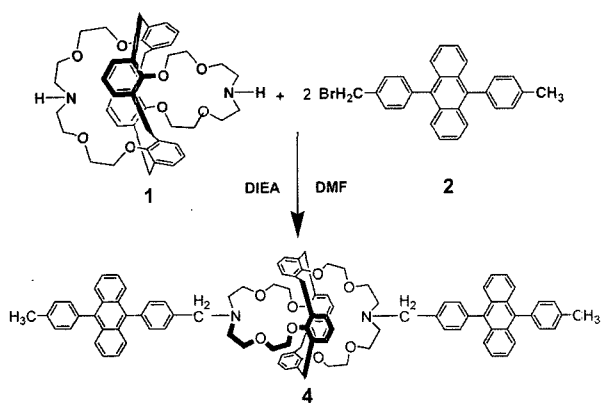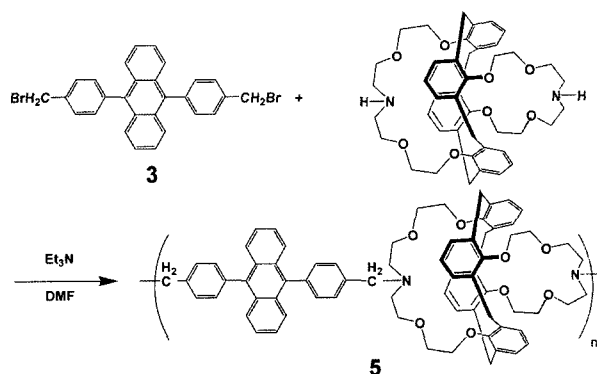
The polymers show good solubility in common organic solvents such as acetone, ethyl acetate, chloroform, methylene chloride and THF, while they display virtually no solubility in *n*-hexane, methanol and ethyl ether.

The condensation polymerization gave the polymers with somewhat small molecular weight judging from the data of viscosity and GPC. The polymers possessed inherent viscosity 0.33 dL/g for 5 using chloroform at 25 °C. The weight average molecular weight determined by GPC using polystyrene standards, of polymer 5 was 12,400 g/mole with a polydispersity index of 1.56. However, these are somewhat high molecular weights judging from viscosity and GPC data. Calix[4]-bis-azacrown-5 moiety often prevents the growing of the molecular weight due to the bulkiness. When films were cast by allowing the solvent of the polymer 5 to evaporate on a glass, hard and brittle films were obtained. Free 4 and 5 exhibited absorption at λ_{max}=372.1 and emission at λ_{max}= 430.1 nm in ethanol, respectively. The absorption bands of the chromoionophores 4 in the visible region are hypsochromically shifted (2-3 nm) by the complexation of alkali and alkaline earth metal ions. The strongest λ_{max} shift is known to be affected by the cation which best fits into the ligand cavity. In donor-acceptor fluorophores, the electronic excitation is mostly accompanied by a charge density shift in the direction of the acceptor substituents of the fluoroionophore, i.e., increases in the dipole moments take place. Since it can be postulated that the amine nitrogen atoms of the fluoroiono-phores (4, 5) are positively polarized, the excited states are more strongly destabilized by cations than the ground states; therefore, hypsochromic shifts result.[1] All titration studies were conducted at around pH 7 using a 6 mM concentration of 4 and polymer 5 using 0.5, 1 and 10 equivalents of these metal ions. Alkali, alkaline earth and various metals including Ag$^+$ and Al^{3+} have been used to evaluate metal ion binding. Emission intensities of model and polymeric fluoroiono-phores containing calix[4]azacrown for various cations are summarized in Table I. Model compound 4 consists of calix [4]-bis-azacrown-5 with two pendent diphenylanthracene groups. 4 displayed a large fluorescence enhancing effect

with K^+ and Rb^+, even though there was a relatively small fluorescence-enhancing effect with Li^+ and Cs^+ ion.

The CHEF (chelation-enhanced fluorescence) effect of the Na^+ ion was negligible compared with that of the K^+ ion. K^+ and Rb^+ ions are known to have effective size for calix[4] azacrown-5. The emission intensity of **4** with increasing amounts of Rb^+, Ag^+ and Al^{3+} ions is shown in Figure 1. Upon the addition of the K^+ and Rb^+ ions (10 equivalents), there were 2.8- and 1.9-fold change in the emission, respectively, as shown in Figure 1(a). Among the investigated metal ions, the stable complexes were obtained for K^+ in
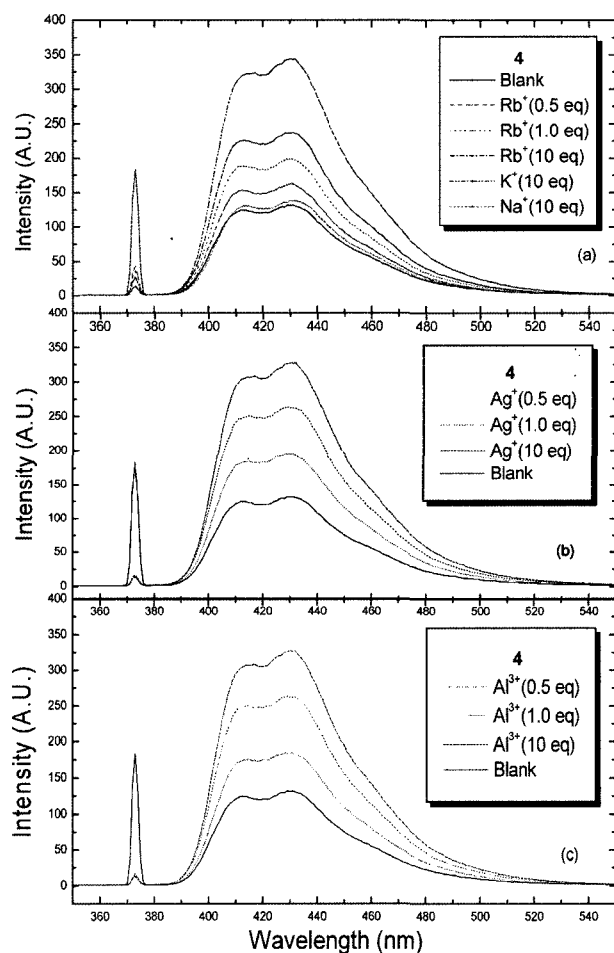
Figure 1. Fluorescence spectra of 4 upon the addition with (a) alkali metal cations, (b) Ag^+, and (c) Al^{3+}.

accordance with the size of these cations with respect to the calix[4]azacrown-5 diameter. Addition of Ca^{2+}, Sr^{2+} and Ba^{2+} also induce emission changes, but the emission intensity is slightly enhanced. As with the Ba^{2+} complex, 1.6-fold emission enhancement was observed. The data indicate that the emission intensity changes appear significantly as concentration of cation increased in ethanol. Using these metal ions, we found that **4** displayed large CHEF effects with Ag^+, Al^{3+} and Y^{3+}.

Very similar results are observed following addition of alkali metal ions Na^+, K^+ and Rb^+ to **5** in ethanol. The sequence of emission intensity for alkali metal cations is $Li^+=Cs^+<Na^+<Rb^+<K^+$ with polymeric fluoroionophore **5** as shown in Figure 2(a). The azacrown cavity (ca. 3.6-4.1 Å) of **5** is relatively larger than the K^+ ion (2.76 Å), it strongly recognizes the K^+ ion not only because of an electrostatic interaction between the azacrown cavity and the K^+ ion but also because of a significant K^+-interaction between the two aromatic rings and the K^+ ion when the calix[4]arene is fixed in the 1,3-alternate conformation.[17,18]

Polymer **5** shows small fluorescence enhancement effects with Ca^{2+}, Cd^{2+} and Mg^{2+} in ethanol. But the cavity size of the calix[4]azacrown-5 frame-work is less suitable to alkali earth metal ion. It has been shown that Mg^{2+}, Ca^{2+} and Sr^{2+} used in the experiments were slightly enhanced for the polymer **5**. Attempts to observe any change in the fluorescence intensity of **5** was performed upon the addition of Ag^+ ion in ethanol. A gradual increase in fluorescent emission was observed when the concentration of Ag^+ ion increased as shown in Figure 2(b). Since K^+ ion binds more tightly than Ag^+ ion, the fluorescence of **5** in the presence of 10 equiv. of K^+ showed no decrease upon the addition of Ag^+ (up to 10 equiv.).

The overall emission changes were dramatic: 6- and 5.3-fold for K^+ and Ag^+, 6.5 for Al^{3+}, and 4.8 for the Y^{3+} ion. We believe we were simply observing fluorescence quenching via a PET process.

In ethanol, the fluorescence of **5** was almost completely quenched via the PET process. Upon the addition of alkali metal ion, the CHEF effect was observed due to the inhibition of the PET mechanism. Upon addition of the strong acid to a solution **4** and **5** in ethanol, the emission is enhanced by a factor of 10 because fluorescence quenching is hindered. When acid was added to a solution containing **5** and Ag^+, we

Table I. Emission Intensity of Blue Fluoroionophore Containing Calix[4]azacrown with Various Cations

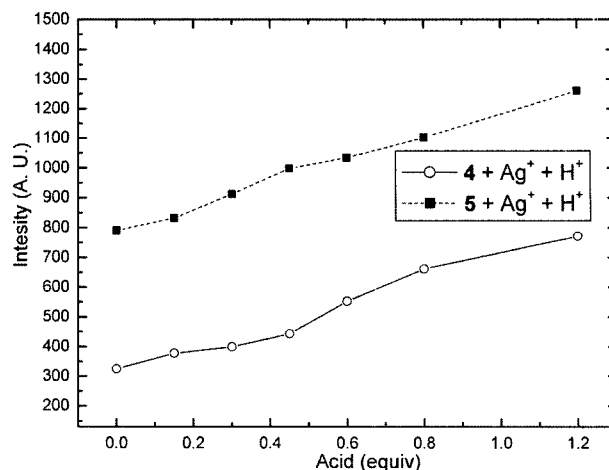| Product	Intensity	1 Group					2 Group				etc.		
	Blank	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ag^+	Al^{3+}	Y^{3+}
4	125	127	131	348	238	128	128	148	167	198	325	327	255
5	148	150	210	890	720	158	152	154	169	500	790	970	710

[4], [5]= 0.06 mM; [Metal perchlorate]= 1.0 mM; absorption, λ_{max}= 372.1 nm; emission, λ_{max}= 430.1 nm.
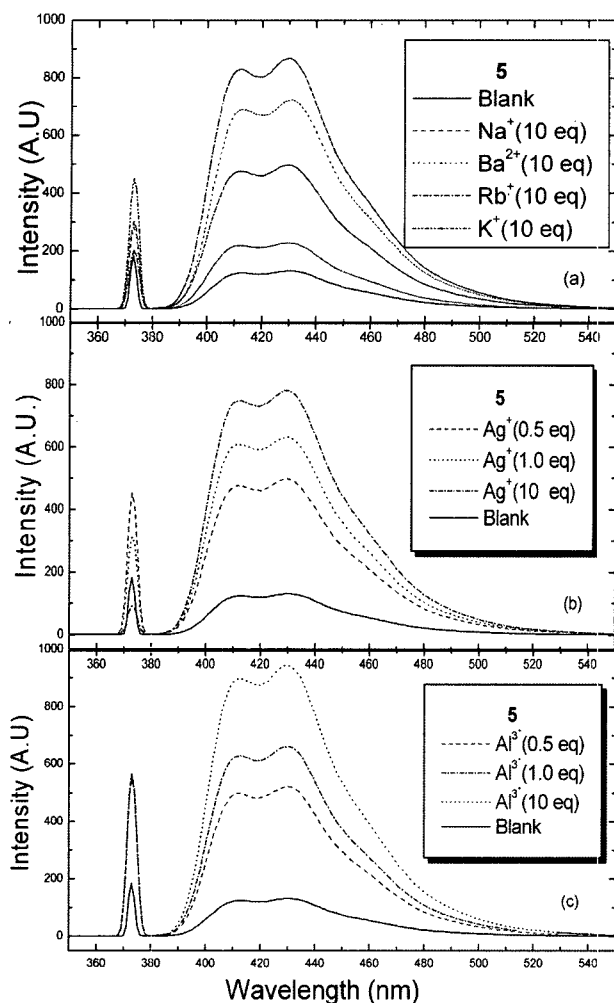
Figure 2. Fluorescence spectra of polymeric fluoroionophore 5 upon the addition with (a) alkali metal and Ba²⁺, (b) Ag⁺ and, (c) Al³⁺.

Figure 3. Fluorescence intensity versus amount of acid for model compound 4 and polymeric fluoroionophore 5.

molecule with a fluorogenic side arm according to the above concept are in progress.

observed strong fluorescence quenching effect with proton as shown in Figure 3. Protonation of amine group of the calix[4]azacrown-5 induced the decomplexation of Ag⁺ from the azacrown-5 site. In the present study, 'the coming in and kicking out' process was easily monitored via fluoresence change. As pH of the solution decreased, the fluorescence intensities of 4 and 5 increased due to the protonation of the tertiary amine group. However, the protonation also caused a slight blue-shift (2-3 nm) in the fluororescence emission of 4 and 5.

In conclusion, we reported synthesis and binding study of new calixarene-based fluoroionophores. Furthermore, the polymeric fluoroionophore with alternating calix[4]azacrown and fluorophore building block can be obtained. By blocking the PET mechanism, we observed up to 6.5-fold emission enhancement in ethanol. Among the metal ions examined, polymer displayed large CHEF effects with K⁺, Ag⁺ and Al³⁺. The design, development, and elucidation of other

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