A calixarene based fluorescent Sr^{2+} and Ca^{2+} probe

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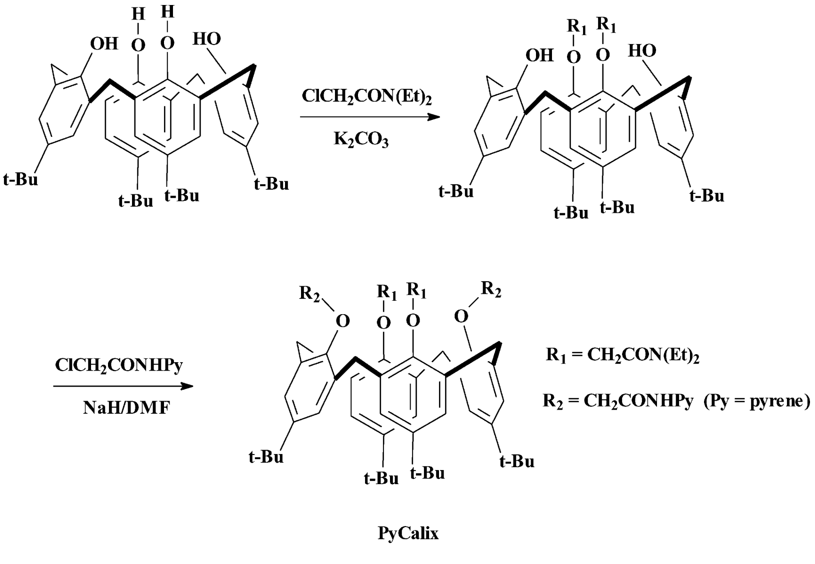
A fluorescent probe, PyCalix, which has two pyrene moieties at the lower rim of a calix[4]arene fixed in the cone conformation was synthesized and its complexation behavior with alkali and alkaline earth cations was studied by fluorescence spectrometry. The compound showed intramolecular excimer emission at approximately 480 nm in the fluorescence spectra. Upon complexation with alkaline earth metal cations, a decrease of excimer emission was observed. The decrease of excimer emission was accompanied by an increase of monomer emission of pyrenes at 397 nm. The order of complexation constants of PyCalix with metal ions was $Sr^{2+} \sim Ca^{2+} > Ba^{2+} > Mg^{2+} > K^+ > Na^+ > Cs^+$ for all reagents. PyCalix doped polyvinyl chloride (PVC) membrane was fabricated and our results showed that this membrane can be used for selective detection of Sr^{2+}.

Radioactive Sr^{2+} is a major component of a "dirty bomb". Highly sensitive and fast detection of Sr^{2+} in the groundwater will help decision making for homeland security and antiterrorist activities. Furthermore, needs exist within Department of Energy for a field instrument to perform real-time characterization and monitoring of radioactive Sr-90 inside high level waste tanks. Fluorescent probes enable researchers to detect a wide range of chemicals from metal ions to complex biomolecular assemblies with exquisite sensitivity and selectivity.[1–3] A few fluorescent Sr^{2+} probes have been demonstrated so far,[4–6] but none of these shows high specificity for Sr^{2+}. Recently, calix[4]arene derivatives bearing amide groups at the lower rim of the ring showed high selectivity to alkaline earth metal ions, and some of them are specific for Sr^{2+}.[7–9] Taking advantages of these results, we report here a new calixarene based fluorescent probe for the detection of Sr^{2+}.

25,27-Bis(*N*,*N*-diethylaminocarbonylmethoxy)-26,28-bis(2-pyryl-aminocarbonylmethoxy)-5,11,17,23-tetrakis-*tert*-butyl-calix[4]arene (PyCalix) was synthesized as shown in Scheme 1. The intermediate 25,27-bis(*N*,*N*-diethylaminocarbonylmethoxy)-5,11,17,23-tetrakis-*tert*-butyl-calix[4]arene was synthesized according to the procedure reported.[10] The structure and purity of PyCalix were determined and ascertained by ^{1}H NMR spectroscopy and mass spectroscopy.[11]

The UV-visible absorption of PyCalix as a function of different concentrations of Sr^{2+} is shown in Fig. 1. No peak shifts or intensity changes of the absorption spectra of PyCalix were observed upon addition of strontium perchloride, suggesting the intramolecular ground state interaction between the two pyrene moieties does not occur.

Fig. 2 shows the fluorescence spectra of PyCalix as a function of concentrations of $Sr(ClO_4)_2$ in acetonitrile at 25 °C. Free PyCalix gave intramolecular excimer emission centered at approximately 480 nm and monomer emission at 397 nm. Upon addition of Sr^{2+} in the solution, the fluorescence peak at 397 nm showed an increase accompanied by a corresponding decrease of the excimer emission at 480 nm. The monomer emission increased when the concentration of Sr^{2+} increased. The increase of monomer emission upon addition of Sr^{2+} will finally cause a complete disappearance of the intramolecular excimer emission. The monomer–excimer



Scheme 1

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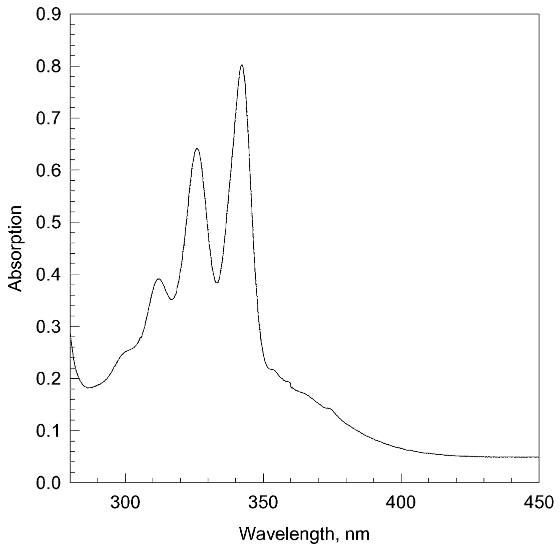


Fig. 1 UV-Visible absorption spectra of PyCalix (1×10^{-5} M in acetonitrile).

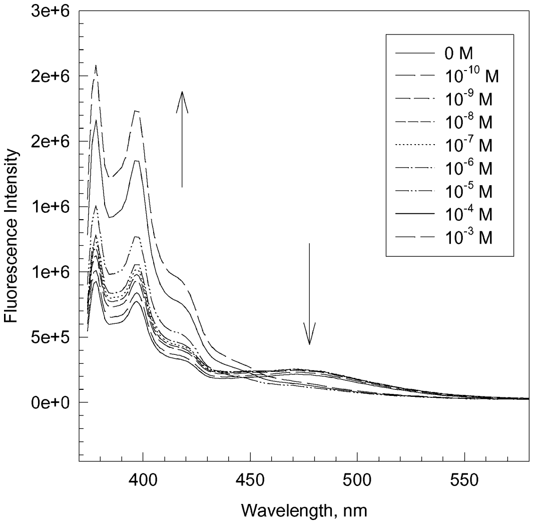


Fig. 2 The changes in the fluorescence spectra of PyCalix (1×10^{-7} M in CH_3CN solution) upon addition of different concentrations of strontium perchlorate, $\lambda_{ex} = 325$ nm.

transformation of pyrenes has been extensively studied before.[12–14] These results clearly indicated the structural change of PyCalix upon complex formation. The two pyrene moieties in a PyCalix were separated by the insertion of Sr^{2+}. An expected structural change of PyCalix before and after the addition of Sr^{2+} is depicted in Scheme 2.

The relative fluorescence intensity ratios of pyrene monomer–excimer emission (I_M/I_E) of PyCalix upon addition of Sr^{2+} are shown in Fig. 3. The I_M/I_E ratio changed from 2.5 to 12 before and after adding 10^{-5}M solution of Sr^{2+}, respectively. The I_M/I_E of PyCalix *vs.* concentrations of different alkali and alkaline metal ions, including Ca^{2+}, Mg^{2+}, Ba^{2+}, Na^+, K^+, and Cs^+ are also shown in Fig. 3. The I_M/I_E *vs.* concentration profile of PyCalix to Ca^{2+} is similar to that of Sr^{2+}. Ba^{2+} gave a similar maximum I_M/I_E ratio, but at higher concentrations (>10^{-4} M). Other metal ions cause no or slight fluorescence change.

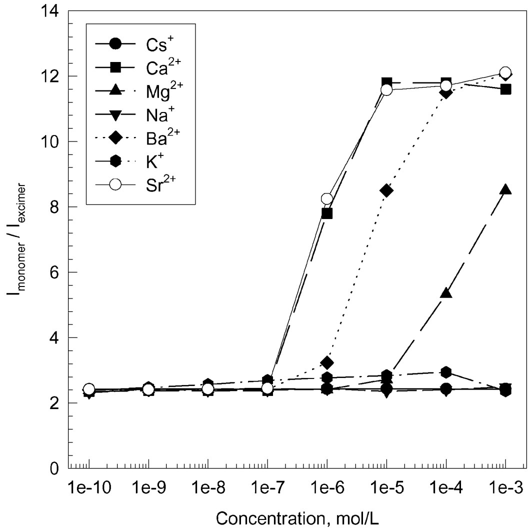
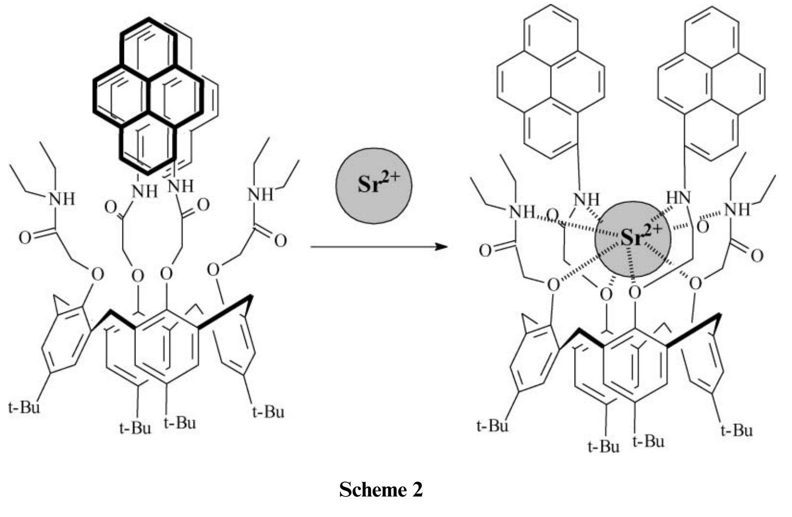


Fig. 3 I_M/I_E of PyCalix (1×10^{-7} M in CH_3CN solution) *vs.* the concentrations of various alkali and alkaline metal ions in perchlorate as the counter anion (acetate for caesium ion). $\lambda_{ex} = 325$ nm.

Metal-ion concentration dependence of the emission intensity (Fig. 3) allowed us to determine the association constant (*K*) by the non-linear curve-fitting method,[15–17] and the data are listed in Table 1. PyCalix shows Sr^{2+} and Ca^{2+} specificity. The order of



Scheme 2

Table 1 Complexation constant of PyCalix with various alkaline and alkali metal ions (in the form of perchlorate) in acetonitrile

	Sr^{2+}	Ca^{2+}	Ba^{2+}	Mg^{2+}	K^+	Na^+	Cs^+
K/L mol^{-1}	1.5×10^6	1.4×10^6	7.0×10^4	6.4×10^3	9.1×10^2	7.6×10^2	—

K value for different metal ions was: $Sr^{2+} \sim Ca^{2+} > Ba^{2+} > Mg^{2+} > K^+ > Na^+ .> Cs^+$. Both I_M/I_E ratios and binding constants show that Ca^{2+} will interfere with the Sr^{2+} recognition, which is because the divalent Ca^{2+} (0.99 Å) and Sr^{2+} (1.13 Å) ions have similar sizes. One possible approach to improve the selectivity in the future is to slightly widen the four amide moieties toward relatively larger Sr^{2+} by removing the steric *tert*-butyl groups from the calixarene.

The sensing behavior of PyCalix in a polymer film was investigated by incorporating PyCalix in a cellulose acetate (CTA) membrane.[18] The 70 μm thickness film was held by two pieces of Teflon plate with a 0.4×0.4 cm^2 window in the middle. The film was placed in a quartz cell for the fluorescence spectra analysis. Fluorescence spectra of PyCalix in the CTA polymer film *vs.* concentration of various metal ions shows similar trend as PyCalix in acetonitrile solution as shown in Fig. 4. These results showed that this PyCalix doped PVC polymer film can be used for selective detection of Sr^{2+}.

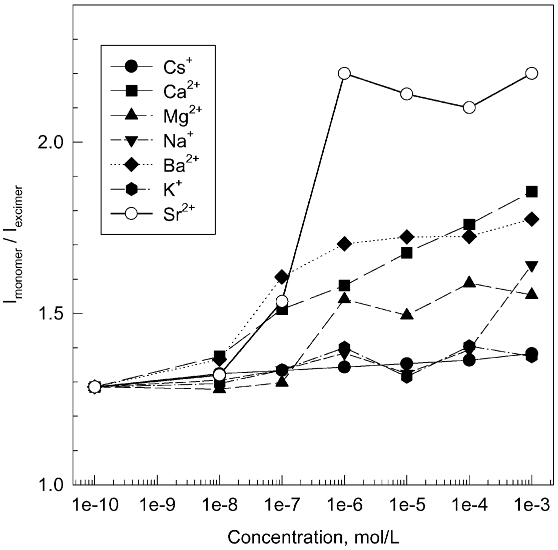


Fig. 4 I_M/I_E of PyCalix in CTA polymer film *vs.* the concentrations of various alkali and alkaline metal ions in water. $\lambda_{ex} = 325$ nm.

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11 25,27-Bis(*N*,*N*-diethylaminocarbonylmethoxy)-5,11,17,23-tetrakis-*tert*-butyl-calix[4]arene (0.5 mmol), 1.25 mmol of *N*-(1-pyryl)-chloroacetamide, and 0.1 g of NaH were mixed in dry DMF (50 ml) at room temperature and stirred for 24 h at room temperature. Water (10 ml) was added slowly to quench the reaction. The solvent then was removed under reduced pressure. The crude product was purified by flash chromatography using methylene chloride as eluant. Yield 26%. $C_{92}H_{102}N_4O_8$, requires: (C, 79.39%; H, 7.39%; O, 9.20%), found: C, 79.20%; H, 6.98%; O, 9.23%; ^{1}H NMR ($CDCl_3$) 7.7–8.3 (m, 18H, pyrene), 6.6–7.0 (m, 8H, Ar-H), 4.7 (s, 4H, pyrene-CH_2), 4.5, 3.2 (two sets of doublets, $2 \times 4H$, $ArCH_2Ar$), 4.4 (s, 4H, CH_2CO), 3.2 (q, 4H, NCH_2CH_3), 1.0 (t, 12H, CH_2CH_3), 0.9, 1.2 (s, $2 \times 18H$, *t*-Bu-CH_3); m/z (1390, M$^+$, 100%).

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18 The film was prepared by combining 4.6 mL of 2.5% cellulose acetate solution in methylene chloride, 0.8 ml of 10^{-5} M of PyCalix solution in methylene chloride, and 0.2 ml of 2-nitrophenyl octyl ether (NPOE). This solution mixture was poured in a flat dish to allow the solvent to evaporate over 24 hours at atmospheric pressure and room temperature. The dish was covered by a watch glass to ensure slow vaporization. The thickness of the film was measured by microscopy to be 70 μm. The transparent film formed was used for the fluorescence study.